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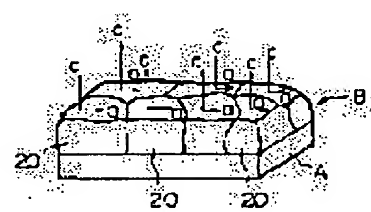
(54) PRODUCTION OF POLYCRYSTALLINE THIN FILM AND PRODUCTION OF OXIDE SUPERCONDUCTOR

(57)Abstract:
PURPOSE: To provide the polycrystalline thin film and oxide superconductor having excellent crystal orientability by depositing constituting particles on a base material while irradiating the film forming surface of a base material with an ion beam at a specific incident angle from a diagonal direction.
CONSTITUTION: Many fine crystal grains 20 having the crystal structure of a cubic crystal system are joined and integrated to each other via crystal grain boundaries in the polycrystalline thin film B formed atop the planar base material A. The C-axes of the crystal axes of the respective crystal grains 20 are directed perpendicularly to the film forming surface of the base body A and the a-axes of the crystal axes of the respective crystal grains 20 are directed to the same direction as each other and are intraplanarly oriented. A target of YSZ is used and the upper surface of a base material holder is irradiated with the ion beams emitted from an ion gun at a 50 to 60° angle at the time of forming the polycrystalline thin film B.



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CLAIMS

[Claim(s)]

[Claim 1] The manufacture method of the polycrystal thin film characterized by beginning to beat the constituent particle of a target by sputtering, making it deposit on a base material, and making the aforementioned constituent particle deposit on a base material, irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material with the degree of incident angle of the range of 50 - 60 degrees in case the aforementioned constituent particle is made to deposit on a base material in the method of forming a polycrystal thin film on a base material.

[Claim 2] In the method of beginning to beat the constituent particle of a target by sputtering, making deposit on a base material, and forming a polycrystal thin film on a base material While making the aforementioned constituent particle deposit on a base material, irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material in case the aforementioned constituent particle is made to deposit on a base material The manufacture method of the polycrystal thin film characterized by making current density of the aforementioned ion beam into two or more 20microA/cm, and making ion beam voltage into less than [700V] more than by 150V.

[Claim 3] The manufacture method of the polycrystal thin film characterized by making into less than 25 degrees the grain-boundary inclination of the crystal grain of the polycrystal thin film which sets the degree of incident angle of an ion beam as the range of 55 - 60 degrees, and is formed on a base material in the manufacture method of a polycrystal thin film according to claim 1.

[Claim 4] the oxide superconductivity characterized by using an inactive gas ion or the mixed ion of inert gas and oxygen gas as ion according to claim 1, 2, or 3 -- the manufacture method of a conductor

[Claim 5] In the manufacture method of a conductor the oxide superconductivity which begins to beat the constituent particle of a target by sputtering, is made to accumulate on a base material, forms a polycrystal thin film on a base material, and forms an oxide superconductivity layer subsequently to this polycrystal thin film top -- Irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material with the degree of incident angle of the range of 50 - 60 degrees, in case the aforementioned constituent particle is made to deposit on a base material, make a spatter particle deposit and a polycrystal thin film is formed. the oxide superconductivity characterized by forming an oxide superconductivity layer on this polycrystal thin film -- the manufacture method of a conductor

[Claim 6] In the manufacture method of a conductor the oxide superconductivity which begins to beat the constituent particle of a target by sputtering, is made to accumulate on a base material, forms a polycrystal thin film on a base material, and forms an oxide superconductivity layer subsequently to this polycrystal thin film top -- While making a spatter particle deposit, irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material in case the aforementioned constituent particle is made to deposit on a base material the oxide superconductivity characterized by forming two or more 20microA/cm for the current density of the aforementioned ion beam, forming a polycrystal thin film for ion

beam voltage as less than [700V] more than by 150V, and forming an oxide superconductivity layer on this polycrystal thin film — the manufacture method of a conductor
[Claim 7] oxide superconductivity according to claim 5 or 6 — the oxide superconductivity characterized by making into less than 25 degrees the grain-boundary inclination of the crystal grain of the polycrystal thin film which sets the degree of incident angle of an ion beam as the range of 55 - 60 degrees, and is formed on a base material in the manufacture method of a conductor — the manufacture method of a conductor
[Claim 8] the oxide superconductivity characterized by growing the crystal of oxides superconductors epitaxially to the crystal of a polycrystal thin film in case an oxide superconductivity layer is formed on a polycrystal thin film according to claim 5, 6, or 7 — the manufacture method of a conductor
[Claim 9] the oxide superconductivity according to claim 5, 6, 7, or 8 characterized by using an inactive gas ion or the mixed ion of inert gas and oxygen gas as ion — the manufacture method of a conductor

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[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] the oxide superconductivity in which the manufacture method of a polycrystal thin film that crystal orientation was ready, as for this invention, and crystal orientation were ready -- it is related with the manufacture method of a conductor
[0002]
[Description of the Prior Art] Although the oxides superconductors become and discovered at recent years are outstanding superconductors which show the critical temperature exceeding liquid nitrogen temperature, in order to use this kind of oxides superconductors as a practical superconductor now, the trouble which should solve various exists. One of the trouble of the is a problem of a low in the critical current density of oxides superconductors.
[0003] Although the problem that the critical current density of the aforementioned oxides superconductors is low is the cause with big an electric anisotropy existing in the crystal of oxides superconductors itself and especially oxides superconductors tend to pass the electrical and electric equipment to a shaft orientations and b shaft orientations of the crystallographic axis, it is known that it will be hard to pass the electrical and electric equipment to c shaft orientations. In order to form oxides superconductors on a base material from such a viewpoint and to use this as a superconductor, it is necessary to form the oxides superconductors of the good state of a crystal stacking tendency on a base material, to make the orientation of the a-axis or b-axis of the crystal of oxides superconductors carry out in the direction which is going to pass the electrical and electric equipment moreover, and to make the orientation of the c axis of oxides superconductors carry out in the direction of other.
[0004] Various meanses have been tried in order to form the good oxide superconductivity layer of a crystal stacking tendency on base materials, such as a substrate metallurgy group tape, conventionally. As the one method, the method of forming an oxide superconductivity layer by the forming-membranes methods, such as sputtering, on these single crystal base materials is enforced using single crystal base materials, such as MgO to which oxides superconductors and the crystal structure were similar, or $SrTiO_3$.
[0005] If the forming-membranes methods, such as sputtering, are performed using Above MgO or the single crystal base material of $SrTiO_3$, in order that the crystal of an oxide superconductivity layer may carry out a crystal growth based on the crystal of a single crystal base material, it is possible to make the crystal stacking tendency good, and it is known that the oxide superconductivity layer formed on these single crystal base materials will demonstrate hundreds of thousands - about two millions A/cm critical current density high enough.
[0006]
[Problem(s) to be Solved by the Invention] By the way, in order to use oxides superconductors as a conductor, it is necessary to form the good oxide superconductivity layer of a crystal stacking tendency on the base material of long pictures, such as the shape of a tape. However, as for the metal tape itself, if an oxide superconductivity layer is directly formed on base materials, such as a metal tape, since it differs from oxides superconductors greatly, the crystal structure cannot form the good oxide superconductivity layer of a crystal stacking tendency at

all by the polycrystalline substance, either. And a diffusion reaction arises between a metal tape and an oxide superconductivity layer with heat treatment performed in case an oxide superconductivity layer is formed, the crystal structure of an oxide superconductivity layer collapses, and there is a problem on which a superconductivity property deteriorates.

[0007] Then, using a sputtering system, covering interlayers, such as MgO and SrTiO3, and forming an oxide superconductivity layer on this interlayer on base materials, such as a metal tape, conventionally, is performed. However, the oxide superconductivity layer formed by the sputtering system on this kind of interlayer had the problem that only low critical current density (for example, thousands – about two 10,000 A/cm) was considerably shown rather than the oxide superconductivity layer formed on the single crystal base material. This is considered to be based on the reason for explaining below.

[0008] the oxide superconductivity which drawing 9 formed the interlayer 2 by the sputtering system on the base materials 1, such as a metal tape, and formed the oxide superconductivity layer 3 by the sputtering system on this interlayer 2 — the cross-section structure of a conductor is shown In the structure shown in drawing 9 , the oxide superconductivity layer 3 is in a polycrystal state, and is in the state where much crystal grain 4 joined together disorderly. If each of such crystal grain 4 is seen separately, although orientation of the c axis of the crystal of each crystal grain 4 is perpendicularly carried out to the base-material front face, an a-axis and a b-axis will be considered to have turned to the disorderly direction.

[0009] Thus, if the sense of an a-axis and a b-axis becomes disorderly for every crystal grain of an oxide superconductivity layer, as a result of [**** in the quantum unity of a superconductivity state] being divided, in the grain boundary to which the crystal stacking tendency was confused, it will be thought that the fall of a superconductivity property, especially critical current density is caused. Moreover, it is thought that the aforementioned oxides superconductors will be in an a-axis and the polycrystal state which has not carried out b-axis orientation for the oxide superconductivity layer 3 growing so that it may have consistency into an interlayer's 2 crystal when forming the oxide superconductivity layer 3, since the interlayer 2 formed in the bottom of it is in an a-axis and the polycrystal state which has not carried out b-axis orientation.

[0010] By the way, the technology which forms various kinds of orientation films on the base material of the polycrystalline substance in addition to the applicable field of the aforementioned oxides superconductors is used. for example, although it is fields, such as a field of an optical thin film, a field of a magneto-optic disk, a field of a wiring substrate, a RF waveguide, and a high pass filter, a cavity resonator, also in which technology, the good polycrystal thin film of the stacking tendency by which membraneous quality was stabilized is formed on a base material — things have been technical problems That is, if quality, such as an optical thin film which will be formed on it if the crystal stacking tendency of a polycrystal thin film is good, a magnetic thin film, and a thin film for wiring, improves and the direct formation of the good optical thin film of a crystal stacking tendency, a magnetic thin film, the thin film for wiring, etc. can be further carried out on a base material, in addition, it will be desirable.

[0011] Moreover, as core material of the magnetic head used in a high-frequency band, it has high permeability and, also thermally, magnetic thin films, such as a stable permalloy or a Sendust, are put in practical use. Although these magnetic thin films were conventionally formed on the predetermined substrate of vacuum evaporationo or the spatter, control of the magnetic anisotropy of a magnetic thin film became it difficult that the stacking tendency of the crystal orientation of these magnetic thin films was a low thing, within the film surface, the direction of crystal grain became disorderly and they had the problem by which the RF property of permeability is spoiled. Moreover, the local fluctuation called a skew and ripple to the magnetization within a field as the shaft orientations of the crystallographic axis within a film surface are disorderly will occur, and the RF property of permeability will be spoiled as mentioned above.

[0012] the oxide superconductivity equipped with offering the polycrystal thin film which could also arrange the a-axis and the b-axis of a crystallographic axis of crystal grain along the field parallel to a membrane-formation side, and was excellent in the crystal stacking tendency, while

it was made in order that this invention might solve the aforementioned technical problem, and orientation of the c axis of a crystallographic axis can be carried out to the right-angle sense to the membrane-formation side of a base material, and the oxide-superconductivity layer excellent in the crystal stacking tendency -- it aims at offering a conductor
[0013]
[Means for Solving the Problem] In the method of beginning to beat the constituent particle of a target by sputtering, making deposit on a base material, and forming a polycrystal thin film on a base material, in order that invention according to claim 1 may solve the aforementioned technical problem The aforementioned constituent particle is made to deposit on a base material, irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material with the degree of incident angle of the range of 50 - 60 degrees, in case the aforementioned constituent particle is made to deposit on a base material.
[0014] In the method of beginning to beat the constituent particle of a target by sputtering, making deposit on a base material, and forming a polycrystal thin film on a base material, in order that invention according to claim 2 may solve the aforementioned technical problem While making the aforementioned constituent particle deposit on a base material, irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material in case the aforementioned constituent particle is made to deposit on a base material Current density of the aforementioned ion beam is made into two or more 20microA/cm, and ion beam voltage is made into less than [700V] or more by 150.
[0015] Invention according to claim 3 makes the grain-boundary inclination of the crystal grain of the polycrystal thin film which sets the degree of incident angle of an ion beam as the range of 55 - 60 degrees, and is formed on a base material less than 25 degrees in the manufacture method of a polycrystal thin film according to claim 1, in order to solve the aforementioned technical problem.
[0016] Invention according to claim 4 uses an inactive gas ion or the mixed ion of inert gas and oxygen gas as ion according to claim 1 or 2, in order to solve the aforementioned technical problem.
[0017] In order to solve the aforementioned technical problem, invention according to claim 5 begins to beat the constituent particle of a target by sputtering, and is made to deposit it on a base material. In the manufacture method of a conductor the oxide superconductivity which forms a polycrystal thin film on a base material, and forms an oxide superconductivity layer subsequently to this polycrystal thin film top -- Irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material with the degree of incident angle of the range of 50 - 60 degrees, in case the aforementioned constituent particle is made to deposit on a base material, make a spatter particle deposit and a polycrystal thin film is formed. An oxide superconductivity layer is formed on this polycrystal thin film.
[0018] In order to solve the aforementioned technical problem, invention according to claim 6 begins to beat the constituent particle of a target by sputtering, and is made to deposit it on a base material. In the manufacture method of a conductor the oxide superconductivity which forms a polycrystal thin film on a base material, and forms an oxide superconductivity layer subsequently to this polycrystal thin film top -- While making a spatter particle deposit, irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material in case the aforementioned constituent particle is made to deposit on a base material Two or more 20microA/cm are formed for the current density of the aforementioned ion beam, a polycrystal thin film is formed for ion beam voltage as less than [700V] or more by 150, and an oxide superconductivity layer is formed on this polycrystal thin film.
[0019] in order that invention according to claim 7 may solve the aforementioned technical problem -- oxide superconductivity according to claim 5 or 6 -- in the manufacture method of a conductor, the grain-boundary inclination of the crystal grain of the polycrystal thin film which sets the degree of incident angle of an ion beam as the range of 55 - 60 degrees, and is formed on a base material is made into less than 25 degrees
[0020] Invention according to claim 8 is the manufacture method of the oxides superconductors

characterized by growing the crystal of oxides superconductors epitaxially to the crystal of a polycrystal thin film in case an oxide superconductivity layer is formed on a polycrystal thin film according to claim 5, 6, or 7, in order to solve the aforementioned technical problem.
[0021] Invention according to claim 9 is the manufacture method of the oxides superconductors according to claim 5, 6, 7, or 8 characterized by using an inactive gas ion or the mixed ion of inert gas and oxygen gas as ion in order to solve the aforementioned technical problem.
[0022]
[Function] As a result of activating a constituent particle efficiently since an ion beam is also simultaneously irradiated from the range of the 50 – 60 directions of slant of a base material in case the spatter particle begun to beat from the target by sputtering is made to deposit on a base material, in addition to a c axis stacking tendency, an a-axis stacking tendency and a b-axis stacking tendency also improve to the membrane formation side of a base material. consequently — even if it is the polycrystal thin film in which much grain boundaries were formed — both the a-axis stacking tendency for every crystal grain a b-axis stacking tendency and a c axis stacking tendency — although — it becomes good and the polycrystal thin film which improved is obtained Moreover, in order to activate the constituent particle in the case of a spatter, the mixed ion of argon ion or argon ion, and oxygen ion is desirable.
[0023] In addition, this inventions assume the following things as a factor in which the crystal stacking tendency of the aforementioned polycrystal thin film is ready. In the unit lattice of the crystal of the cubic polycrystal thin film formed on the substrate, the directions of a substrate normal are <100> shafts, and each of other <010> shafts and <001> shafts serves as a direction which intersects perpendicularly with <100> shafts. If the ion beam which carries out incidence from across to a substrate normal is taken into consideration to these directions, when carrying out incidence along the direction of the diagonal line of a unit lattice, i.e., <111> shafts, to the zero of a unit lattice, it becomes the 54.7 degrees of incident angle. That a good crystal stacking tendency is shown here in the range whose degree of incident angle of an ion beam is 50 – 60 degrees as mentioned above The degree of incident angle of an ion beam is considered that the bird clapper is related before and after it in accordance with the 54.7 aforementioned degrees. In the crystal which ion channeling took place most effectively when these angles were in agreement or having been approximated, and has been deposited on a base material Only the atom which became the arrangement relation which is in agreement with the aforementioned angle on the upper surface of a base material becomes easy to remain alternatively. As a result of a spatter's being carried out by the spatter effect which the ion beam by which incidence is carried out aslant generates and being removed, only the crystal into which the good atoms of a stacking tendency gathered remained alternatively, and deposited the thing of the atomic arrangement to which others were confused, this became a cause and it presumes that in which a crystal stacking tendency is ready.
[0024] Therefore, if too low, it will become the shortage of ion irradiation, the aforementioned effect is made hard to produce, and when ion beam voltage is too high, it will produce the spatter effect conversely and will disturb a crystal stacking tendency. As for the current density of the above thing to an ion beam, it is desirable to consider as two or more 20microA/cm, and, as for ion beam voltage, it is desirable to consider as less than [700V] more than by 150V.
[0025] Moreover, if an oxide superconductivity layer is grown epitaxially on the good polycrystal thin film of the aforementioned crystal stacking tendency, as a result of an oxide superconductivity layer's carrying out a crystal growth along with the crystal of a polycrystal thin film, what has an a-axis stacking tendency, a b-axis stacking tendency, and a c axis stacking tendency good [an oxide superconductivity layer] is obtained.
[0026]
[Example] Hereafter, the example of this invention is explained with reference to a drawing. The polycrystal thin film by which A was formed in the base material of a tabular and B was formed [in / drawing 1 / drawing 1 shows one example in which the polycrystal thin film of this invention was formed on the base material, and] in the upper surface of a base material A is shown. The aforementioned base material A can use the thing of various configurations, such as a plate, a wire rod, and tape material, and a base material A consists of metallic materials, such

as silver, platinum, stainless steel, and copper, an alloy, various glass or various ceramics, etc.
[0027] It comes to carry out junction unification through the grain boundary, and the c axis of the crystallographic axis of each crystal grain 20 is turned right-angled to the upper surface (membrane formation side) of a base material A, the a-axes and b-axes of a crystallographic axis of each crystal grain 20 are mutually turned in the same direction, and orientation within a field of much detailed crystal grain 20 in which the aforementioned polycrystal thin film B has the crystal structure of cubic system is carried out mutually. Moreover, orientation of the c axis of each crystal grain 20 is carried out right-angled to the membrane formation (upper surface) side of a base material A. And the a-axes (or b-axis) of each crystal grain 20 make those angles (the grain-boundary inclination K shown in drawing 2) to make less than 30 degrees, and junction unification is carried out.
[0028] Next, the equipment which manufactures the aforementioned polycrystal thin film B is explained. Drawing 3 shows an example of equipment which manufactures the aforementioned polycrystal thin film B, and the equipment of this example has the composition of having prepared the ion gun for ion beam assistance in the sputtering system.
[0029] The target 12 of a tabular with which opposite arrangement of the equipment of this example was carried out with the predetermined interval in the slanting upper part of the base-material electrode holder 11 which holds a base material A horizontally, and this base-material electrode holder 11, The spatter beam irradiation equipment 14 which the slanting upper part of the aforementioned base-material electrode holder 11 was countered with the predetermined interval, and the ion gun 13 which estranged with the target 12 and has been arranged, and the aforementioned target 12 set caudad, and has been arranged towards the inferior surface of tongue of a target 12 is constituted as a subject. Moreover, the sign 15 in drawing shows the target electrode holder holding the target 12.
[0030] Moreover, the equipment of this example is contained by the vacuum housing of illustration abbreviation, and can hold the circumference of a base material A now in vacuum atmosphere. Furthermore, controlled-atmosphere sources of supply, such as a chemical cylinder, are connected to the aforementioned vacuum housing, and it can be made the inert gas atmosphere which is in low voltage states, such as a vacuum, about the interior of a vacuum housing, and contains the inert gas atmosphere or oxygen of argon gas or others now.
[0031] In addition, when using a long metal tape (tapes, such as a product made from a Hastelloy, or a product made from stainless steel) as a base material A, it is desirable to constitute so that continuation membrane formation of the polycrystal thin film can be carried out on a tape-like base material by forming the sending-out equipment and take-up motion of a metal tape in the interior of a vacuum housing, and sending out a base material A and rolling round to the base-material electrode holder 11 with take-up motion continuously from sending-out equipment. The aforementioned base-material electrode holder 11 equips the interior with a heating heater, and can heat now the base material A located on the base-material electrode holder 11 to the temperature of business. Moreover, the angle adjustment mechanism D is attached to the pars basilaris ossis occipitalis of the base-material electrode holder 11. This angle adjustment mechanism D is constituted considering the pedestal 7 which supports the up support plate 5 joined to the pars basilaris ossis occipitalis of the base-material electrode holder 11, the lower support plate 6 by which pin combination was carried out at this up support plate 5, and this lower support plate 6 as a subject. The aforementioned up support plate 5 and the lower support plate 6 are mutually constituted free [rotation] through a part for a pin bond part, and can adjust now the level angle of the base-material electrode holder 11. In addition, although the angle adjustment mechanism D in which the angle of the base-material electrode holder 11 was adjusted was established in this example, the angle adjustment mechanism D is attached in the ion gun 13, the degree of tilt angle of the ion gun 13 is adjusted, and you may make it adjust the degree of incident angle of an ion beam. Moreover, an angle adjustment mechanism cannot be restricted to the composition of this example, and, of course, the thing of various composition can be adopted.
[0032] The aforementioned target 12 is for forming the polycrystal thin film made into the purpose, and the thing of the same composition as the polycrystal thin film of the target

composition or approximation composition etc. is used for it. What is necessary is not to restrict to this, although the zirconia (YSZ) specifically stabilized by MgO or Y2O3, MgO, SrTiO3, etc. are used as a target 12, and just to use TAGETSU corresponding to the polycrystal thin film which it is going to form.
[0033] Inside the container, the aforementioned ion gun 13 contains an evaporation source, pulls it out near the evaporation source, is equipped with an electrode and constituted. And it is equipment which it controls by the electric field which ionized a part of atom generated from the aforementioned evaporation source, or molecule, pulled out the ionized particle, and were generated in the electrode, and is irradiated as an ion beam. There are various things, such as a direct-current-discharge method, a RF excitation method, a filament formula, and a cluster ion beam method, in ionizing a particle. A filament formula is the method of carrying out energization heating at the filament made from a tungsten, making generate a thermoelectron, making collide with an evaporation particle in a high vacuum, and ionizing. Moreover, from the nozzle prepared in opening of the crucible to which the raw material was paid, by the thermoelectron, a cluster ion beam method carries out the shock of the cluster of the set molecule which comes out in a vacuum, ionizes it, and emits it. In this example, the ion gun 13 of the internal structure of composition of being shown in drawing 4 (a) is used. This ion gun 13 is constituted in preparation for the interior of the tubed container 16 in the drawer electrode 17, a filament 18, and the introductory pipes 19, such as Ar gas, and can irradiate ion in parallel with the shape of a beam from the nose of cam of a container 16.
[0034] As shown in drawing 3 , the aforementioned ion gun 13 has the medial axis S, made it incline to the upper surface (membrane formation side) of a base material A with the degree theta of incident angle (angle of the perpendicular (normal) of a base material A, and a center line S to make), and has countered. Although this degree theta of incident angle has the desirable range of 50 - 60 degrees, the range of 55 - 60 degrees is the most desirable. Therefore, the ion gun 13 is arranged so that it may have with a tilt angle theta to the upper surface of a base material A and the incidence of the ion beam can be carried out. In addition, the ion beam which irradiates a base material A according to the aforementioned ion gun 13 is good at the ion beam of rare gas, such as helium+, Ne+, Ar+, Xe+, and Kr+, or the mixed ion beam of them and oxygen ion. in order to prepare the crystal structure of a polycrystal thin film, a certain amount of atomic weight is required, and when it takes into consideration that it is thin ineffective with too much lightweight ion, it is desirable [it is **, and] to use ion, such as Ar+ and Kr+
[0035] The aforementioned spatter beam irradiation equipment 14 irradiates an ion beam in composition equivalent to the ion gun 13 to nothing and a target 12, and can begin to beat the constituent particle of a target 12. In addition, with this invention equipment, since it is important that the constituent particle of a target 13 can be begun to beat, the seal of approval of the voltage is carried out to a target 12 by the high frequency coil etc., the constituent particle of a target 12 may be begun to beat, and it may constitute so that it may be possible, and the spatter beam irradiation equipment 14 may be omitted.
[0036] Next, the case where the polycrystal thin film B of YSZ is formed on a base material A using the equipment of the aforementioned composition is explained. In order to form the polycrystal thin film B on a base material A, while using the target of YSZ, it enables it to irradiate the ion beam which the angle adjustment mechanism D is adjusted and is irradiated from the ion gun 13 at an angle of the range of 50 - 60 degrees on the upper surface of the base-material electrode holder 11. Next, vacuum length of the interior of the container which has contained the base material A is carried out, and it considers as reduced pressure atmosphere. And the ion gun 13 and the spatter beam irradiation equipment 14 are operated.
[0037] If an ion beam is irradiated from the spatter beam irradiation equipment 14 at a target 12, the constituent particle of a target 12 will be begun to beat, and it will come flying on a base material A. And the mixed ion beam of Ar ion and oxygen ion is irradiated from the ion gun 13 at the same time it makes the constituent particle begun to beat from the target 12 deposit on a base material A. The degree theta of incident angle at this time of carrying out ion irradiation has 50 - 60 most desirable degrees. If theta is made into 90 degrees here, although orientation of the

c axis of a polycrystal thin film is carried out right-angled to the membrane formation side of a base material A, since a field (111) stands on the membrane formation side of a base material A, it is not desirable. Moreover, if theta is made into 30 degrees, a polycrystal thin film will not carry out even c axis orientation. If ion beam irradiation is carried out at an angle of the above desirable ranges, the field (100) of the crystal of a polycrystal thin film will come to stand.
[0038] Although orientation of the a-axis and b-axis of a crystallographic axis of YSZ which are formed on a base material A can be carried out by performing sputtering, performing ion beam irradiation with such a degree of incident angle, it is thought that this is based on the result efficiently activated by having carried out ion beam irradiation at the suitable angle to the spatter particle in the middle of having deposited. [of a polycrystal thin film]
[0039] In addition, this inventions assume the following things as a factor in which the crystal stacking tendency of this polycrystal thin film B is ready. The unit lattice of the crystal of the polycrystal thin film B of YSZ is a cubic as shown in drawing 4 (b), in this crystal lattice, the directions of a substrate normal are <100> shafts, and each of other <010> shafts and <001> shafts serves as a direction shown in drawing 4 (b). If the ion beam which carries out incidence from across to a substrate normal is taken into consideration to these directions, when carrying out incidence along the direction of the diagonal line of a unit lattice, i.e., <111> shafts, to the zero O of drawing 4 (b), it becomes the 54.7 degrees of incident angle. That a good crystal stacking tendency is shown in the range of the 50 - 60 degrees of incident angle as mentioned above here In the crystal which ion channeling took place most effectively and has deposited on a base material A when the degree of incident angle of an ion beam comes before and after it in accordance with the 54.7 aforementioned degrees Only the atom which became the arrangement relation which is in agreement with the aforementioned angle on the upper surface of a base material A becomes easy to remain alternatively. The thing of the atomic arrangement to which others were confused presumes what only the crystal into which the good atoms of a stacking tendency gathered remains alternatively, and deposits, as a result of a spatter's being carried out by the spatter effect of an ion beam and being removed.
[0040] The aforementioned effect is made hard to become the shortage of ion irradiation and to produce from the above thing, if the ion beam voltage at the time of irradiating an ion beam is too low, and when too high, conversely, the spatter effect becomes high and will disturb a crystal stacking tendency. As for the current density of the above thing to an ion beam, it is desirable to consider as two or more 20microA/cm, and, as for ion beam voltage, it is desirable to consider as less than [700V] more than by 150V.
[0041] The base material A which the polycrystal thin film B of YSZ deposited on drawing 1 and drawing 2 by the aforementioned method is shown. In addition, although drawing 1 shows the state where one layer of crystal grain 20 was formed, of course, it does not interfere by the multilayer structure of crystal grain 20.
[0042] next, the oxide superconductivity which drawing 5 and drawing 6 require for this invention — what shows one example of a conductor — it is — the oxide superconductivity of this example — the conductor 23 consists of an oxide superconductivity layer C formed in the upper surface of the polycrystal thin film B formed in the upper surface of the base material A of a tabular, and this base material A, and the polycrystal thin film B The aforementioned base material A and the polycrystal thin film B consist of material equivalent to the material explained in the previous example, and crystal orientation of the crystal grain 20 of the polycrystal thin film B is carried out so that it may become less than 30 grain-boundary inclinations, as shown in drawing 1 and drawing 2 .
[0043] Next, the oxide superconductivity layer C is covered by the upper surface of the polycrystal thin film B, orientation of the c axis of the crystal grain 23 is carried out right-angled to the upper surface of the polycrystal thin film B, orientation within a field is carried out along a field parallel to the base-material upper surface like the polycrystal thin film B of the crystal grain 23 — which explained the a-axis and the b-axis previously, and grain-boundary inclination K' which crystal grain 23 form is made into less than 30 degrees. The oxides superconductors which constitute this oxide superconductivity layer Composition Y1Ba2Cu3Ox, Y2Ba4Cu8Ox, and Y3Ba3Cu6Ox — Or (Bi, Pb) 2calcium2Sr2Cu3Ox, composition which becomes 4 Ox 3 Cu 2 Sr 2

(Bi, Pb) calcium, or Tl2Ba2calcium2Cu3Ox, Tl1Ba2calcium2Cu3Ox, and Tl1Ba2calcium3Cu4Ox — they are oxides superconductors with the high critical temperature represented by composition etc.
[0044] Next, the equipment which forms the oxide superconductivity layer C is explained. Drawing 7 shows an example of the equipment which forms an oxide superconductivity layer by the forming-membranes method, and drawing 7 shows laser vacuum evaporationo equipment. The laser vacuum evaporationo equipment 30 of this example has the processing container 31, and can install now a base material A and a target 33 in the vacuum evaporationo processing room 32 inside this processing container 31. That is, while a pedestal 34 is formed in the pars basilaris ossis occipitalis of the vacuum evaporationo processing room 32 and being able to install a base material A in the upper surface of this pedestal 34 in the level state, the target 33 supported by the support electrode holder 36 is formed in the slanting upper part of a pedestal 34 in the state of the inclination. It connects with the evacuation equipment of illustration abbreviation through an exhaust hole 37, and the processing container 31 can decompress the interior now to a predetermined pressure.
[0045] The aforementioned target 33 consists of boards, such as a sintered compact of equivalent to the oxide superconductivity layer C which it is going to form, or the multiple oxide which made much approximated composition or many components which are easy to flee during membrane formation contain, or oxides superconductors. The aforementioned pedestal 34 is what built in the heating heater, and can heat a base material A now to desired temperature.
[0046] Laser luminescence equipment 38, the 1st reflecting mirror 39, a condenser lens 40, and the 2nd reflecting mirror 41 are formed in the side of the processing container 31, and it has come to be, able to carry out the convergent radiotherapy of the laser beam which laser luminescence equipment 38 generated to a target 33 on the other hand through the transparent aperture 42 in which it was attached by the side attachment wall of the processing container 31. As long as laser luminescence equipment 38 can begin to beat a constituent particle from a target 33, it may use which things, such as an YAG laser, a CO2 laser, and an excimer laser.
[0047] Next, the case where the oxide superconductivity layer C is formed on the polycrystal thin film B of Above YSZ is explained. If the polycrystal thin film B of YSZ is formed on a base material A as mentioned above, an oxide superconductivity layer will be formed on this polycrystal thin film B. When forming an oxide superconductivity layer on the polycrystal thin film B, in this example, the laser vacuum evaporationo equipment 30 shown in drawing 7 is used.
[0048] It installs on the pedestal 34 of the laser vacuum evaporationo equipment 30 which shows the base material A in which the polycrystal thin film B was formed to drawing 7 , and the vacuum evaporationo processing room 32 is decompressed with a vacuum pump. Oxygen gas is introduced into the vacuum evaporationo processing room 32 here if needed, and it is good also considering the vacuum evaporationo processing room 32 as an oxygen atmosphere. Moreover, the heating heater of a pedestal 34 is operated and a base material A is heated to desired temperature.
[0049] Next, the convergent radiotherapy of the laser beam which made it generate from laser luminescence equipment 38 is carried out to the target 33 of the vacuum evaporationo processing room 32. By this, whether the constituent particle of a target 33 begin to be scooped out evaporates, and the particle deposits on the polycrystal thin film B. Since the polycrystal thin film B carries out c axis orientation beforehand and is carrying out orientation also of an a-axis and the b-axis in the case of deposition here of a constituent particle, it grows epitaxially and crystallizes so that the c axis, a-axis, and b-axis of the crystal of the oxide superconductivity layer C which are formed on the polycrystal thin film B may also be adjusted in the polycrystal thin film B. The good oxide superconductivity layer C of a crystal stacking tendency is obtained by this.
[0050] Although the oxide superconductivity layer C formed on the aforementioned polycrystal thin film B will be in a polycrystal state, in each of the crystal grain of this oxide superconductivity layer C, as shown in drawing 6 , the c axis which cannot pass the electrical and electric equipment easily in the thickness direction of a base material A carries out orientation of it, and a-axes or b-axes are carrying out orientation to the longitudinal direction of

a base material A. Therefore, the obtained oxide superconductivity layer is excellent in the quantum unity in the grain boundary, since there is little degradation of the superconductivity property in the grain boundary, it is easy to pass the electrical and electric equipment in the direction of a field of a base material A, and what was excellent in critical current density is obtained.
[0051] On the other hand, drawing 8 shows other examples of the equipment for manufacturing a polycrystal thin film. The same sign is given to a component equivalent to the equipment indicated to drawing 3 in the equipment of this example, and those explanation is omitted. Differing from the equipment shown in drawing 3 in the equipment of this example is the point of having formed three targets 12, having formed three spatter beam irradiation equipments 14, and having connected RF generator 29 to the base material A and the target 12.
[0052] With the equipment of this example, since begin to beat the particle of another kind, respectively, it is made to deposit on a base material A and a bipolar membrane can be formed from three targets 12, 12, and 12, there is the feature which can also manufacture the polycrystal film of more complicated composition. Moreover, RF generator 30 can be operated and a spatter can also be carried out from a target 12. When enforcing the aforementioned method using the equipment of this example, the polycrystal thin film which was excellent in the stacking tendency like the case of the equipment shown in drawing 3 can be obtained.
[0053] (Example of manufacture) The equipment of composition of being shown in drawing 3 was used, vacuum length of the interior of a container which contained this equipment was carried out with the vacuum pump, and it decompressed to 3.0x10 to 4 torrs. The base material used Hastelloy C276 tape with 0.5mm [in width of face of 10mm, and thickness], and a length of 10cm. The target set the degree of incident angle of the beam of spatter voltage 1000V, 100mA of spatter current, and the ion source as 55 degrees using the thing made from YSZ (stabilized zirconia), the assistant voltage of the ion source was set as 300V, the current density of an ion beam was set as 10-70microA/cm2, respectively, on the base material, ion irradiation was performed simultaneously with sputtering and the YSZ layer of the shape of a film with a thickness of 0.3 micrometers was formed. The current density of the aforementioned ion beam is based on the count value of the current density metering device grounded near the sample here.

[0054] The X diffraction examination by the theta-2theta method for having used CuK alpha rays about each obtained polycrystal thin film sample of YSZ was performed. Drawing 10 - drawing 13 are drawings showing 55 incident angles of the ion source, and the diffraction strength of the sample which measured the current density of an ion beam by ion beam voltage 300V, respectively to 10microA/cm2, 20microA/cm2, 40microA/cm2, and 70microA/cm2. From the result shown in drawing 10 - drawing 13 , the current density of an ion beam by the sample set as 20-70microA/cm2 The peak of the field (200) of YSZ or (400) a field is accepted, and that in which the field (100) of the polycrystal thin film of YSZ is carrying out orientation along the field parallel to a base-material front face can be presumed. It became clear that the polycrystal thin film of YSZ carries out orientation of the C shaft at right angles to the base-material upper surface, and is formed. In addition, the peak of YSZ is not seen if it is in the sample which made ion beam current density 10microA/cm2 from the result shown in drawing 10 . Therefore, when ion beam current density was too low, it became clear that control of the crystal stacking tendency of a polycrystal thin film cannot be performed.
[0055] Then, drawing 14 - drawing 17 show the pole figure in each aforementioned sample. By the sample which made current density of an ion beam 10microA/cm2, a c axis stacking tendency was not seen but the result shown in drawing 10 - drawing 13 and the equivalent result were obtained so that clearly from these drawings. It became clear that the current density at the time of irradiating an ion beam from the above thing is two or more 20microA/cm need.
[0056] Drawing 18 - drawing 20 are drawings showing the diffraction strength of the sample which changed ion beam voltage and ion beam current suitably, and measured them with the 90 degrees of incident angle of the ion source. The beam current shown in each drawing here shows the current for loads of the ion gun used for the experiment. From the result shown in drawing 18 - drawing 20 , even if it set the degree of incident angle of the ion source as 90 degrees, the

peak (200) and peak (400) of YSZ could be accepted, and sufficient stacking tendency was accepted about the c axis stacking tendency.
[0057] Next, in each sample by which c axis orientation was carried out as mentioned above, it measured whether the a-axis or b-axis of a YSZ polycrystal thin film would carry out orientation. For the measurement, as shown in drawing 21 , while irradiating an X-ray at an angle theta at the polycrystal thin film of YSZ formed on the base material A In the vertical plane containing an incidence X-ray, install the X-ray counter 25 in the position of the angle of 2theta (58.7 degrees) to an incidence X-ray, and the value of the level angle phi to the vertical plane containing an incidence X-ray is changed suitably. That is, the stacking tendency of the a-axes of the polycrystal thin film B or b-axes was measured by measuring the diffraction strength obtained when only an angle of rotation phi makes it rotate as a base material A is shown in an arrow in drawing 21 . The result is shown in drawing 22 and drawing 23 .
[0058] When a diffraction peak does not appear in the case of the sample which set the degree of incident angle of an ion beam as 55 degrees, and manufactured it as shown in drawing 22 , but phi is made into 90 degrees and 0 times, the peak of the field (311) of YSZ has appeared every 90 degrees to the angle of rotation phi. This is equivalent to the peak (011) of YSZ within a substrate side, and it became clear that the a-axes or b-axes of a YSZ polycrystal thin film is carrying out orientation. On the other hand, as shown in drawing 23 , in the case of the sample which set the degree of ion beam incident angle as 90 degrees, and manufactured it, a special peak was not seen but that it is disorderly made an a-axis and b shaft orientation clear.
[0059] It became clear that the polycrystal thin film of the sample manufactured by the aforementioned equipment from the above result is carrying out orientation of a-axes and the b-axes as well as c axis orientation. Therefore, it became clear that polycrystal thin films, such as YSZ excellent in the stacking tendency, can be manufactured.
[0060] On the other hand, drawing 24 shows the result which examined the crystal stacking tendency in each crystal grain of the polycrystal layer of this sample using the sample of a YSZ polycrystal thin film used by drawing 22 . In this examination, when performing an X diffraction by the method previously explained based on drawing 21 , the diffraction peak at the time of setting the angle of phi as the value of serration 5 times to -ten - 45 degrees is measured. Although the diffraction peak of the polycrystal thin film of YSZ obtained from the result shown in drawing 24 appears in less than 30 grain-boundary inclinations, its having disappeared is clear at 45 degrees. Therefore, having fitted in less than 30 degrees made clear the grain-boundary inclination of the crystal grain of the obtained polycrystal thin film, and it became clear to have a good stacking tendency.
[0061] Next, ion beam voltage was set as each value of 500V, 700V, 200V, and 150V on conditions almost equivalent to the aforementioned manufacture conditions, and the X diffraction examination was performed about the sample which set the current density of an ion beam as each value of 40microA/cm2, 50microA/cm2, 20microA/cm2, and 30microA/cm2, and manufactured it. Those results are shown in drawing 25 - drawing 29 .
[0062] Moreover, the relation of the above ion beam voltage and ion beam current density which were obtained from the test result shown in drawing 25 - drawing 29 , and the relevance of the crystal stacking tendency of a polycrystal thin film are shown in drawing 30 . From the result shown in drawing 30 , even if each of ion beam voltage and ion beam current density is too high and it is too low, it is unsuitable, it is more than 150V, and ion beam voltage needs to be fewer than 700V, and it became clear that the current density of an ion beam is required for two or more 20microA/cm.
[0063] Next, the current density of 300V and an ion beam is set as 40microA/cm2, ion beam energy is set as 300eV for ion beam voltage, and when the degree of incident angle of an ion beam is changed to zero - 65 degrees and a polycrystal thin film is manufactured, the relation between the degree of incident angle in the distribution of the direction (111) of the crystal of the obtained polycrystal thin film and full width at half maximum is shown. In addition, all the aforementioned half-the-price values asked for the pole figure as shown in drawing 16 about each obtained sample, and when the auxiliary wires e and f as shown in drawing 16 from the center of this pole figure were drawn, they asked for it, the half angle, i.e., the peak ratio half, of

the angle alpha which these auxiliary wires e and f make. The bird clapper became [the crystal stacking tendency] clear good in the range whose degree of incident angle of the result shown in drawing 31 to an ion beam is 50 – 60 degrees. Moreover, it also became clear by making the degree of incident angle of an ion beam into 55 – 60 degrees especially that a grain-boundary inclination is made to the minimal value of about 25 degrees.
[0064] Next, the oxide superconductivity layer was formed using the laser vacuum evaporationo equipment of composition of being shown in drawing 7 on the aforementioned polycrystal thin film. as a target — Y0.7Ba1.7Cu 3.0O7-x — the target which consists of oxides superconductors of composition was used Moreover, the interior of a vacuum evaporationo processing room was decompressed to 10 to 6 torrs, and laser vacuum evaporationo was performed at the room temperature. ArF laser with a wavelength of 193nm was used as laser for target evaporation. Then, it heat-treated in 60 minutes and in oxygen atmosphere by 400 degreeC. The obtained oxides superconductors are things with a width of face [of 0.5mm], and a length of 10cm.
[0065] this oxide superconductivity — the result which cooled the conductor and performed measurement of critical temperature and critical current density — critical temperature =90K Critical-current-density =500000 A/cm2 was shown, and it has checked demonstrating a very excellent superconductivity property.
[0066]
[Effect of the Invention] As a result of being able to activate a constituent particle efficiently since an ion beam is irradiated at the angle of 50 – the 60 directions of slant in case the constituent particle begun to beat from the target by sputtering is made to deposit on a base material as explained above according to the manufacture method of the polycrystal thin film of this invention, the polycrystal thin film of 30 or less grain-boundary inclinations which also raised the a-axis stacking tendency and the b-axis stacking tendency to the membrane formation side of a base material in addition to the c axis stacking tendency can be obtained. Furthermore, a crystal stacking tendency can be prepared still better by making the degree of incident angle of an ion beam into 55 – 60 degrees, and the polycrystal thin film of the good crystal stacking tendency of less than 25 grain-boundary inclinations can be obtained. The aforementioned polycrystal thin film has a good stacking tendency within a field in the a-axis and b-axis of crystal grain which constitute a polycrystal thin film since the diffraction peak of the X diffraction which is made to rotate it and is acquired appears every 90 degrees, and since the appearance range of the peak turns into the range of 0 – 30 degrees, it is also clear that the grain-boundary inclination is 30 degrees.
[0067] Moreover, the polycrystal thin film of a good crystal stacking tendency can be certainly manufactured by setting current density of the ion beam at the time of manufacture of a polycrystal thin film to 20-micrometerA/two or more cm, and making ion beam voltage fewer than more than 150V and 700V. In addition, the ion used as an ion beam has an inactive gas ion or an inactive gas ion, and the mixed desirable ion of oxygen gas.
[0068] Next, according to the manufacture method of the oxides superconductors concerning this invention, the good polycrystal thin film of the above crystal stacking tendencies is formed with 50 – the 60 degrees of incident angle of an ion beam on a base material, and an oxide superconductivity layer is formed on it. The aforementioned polycrystal thin film has the good stacking tendency within a field of the crystal grain which constitutes a polycrystal thin film since the diffraction peak of the X diffraction which is made to rotate it and is acquired appears every 90 degrees, and since it generates an oxide superconductivity layer on it, it can form the good oxide superconductivity layer of a crystal stacking tendency. therefore — since the sense of the a-axes of the crystal grain of an oxide superconductivity layer or b-axes can also be arranged — the high oxide superconductivity of critical current density — a conductor can be obtained furthermore, the oxide superconductivity which was further excellent in the crystal stacking tendency since the crystal stacking tendency could be prepared still better by making the degree of incident angle of an ion beam into 55 – 60 degrees and the polycrystal thin film of the good crystal stacking tendency of less than 25 grain-boundary inclinations was obtained — a conductor can be obtained
[0069] moreover, the thing for which the polycrystal thin film of a good crystal stacking tendency

can be manufactured certainly, and an oxide superconductivity layer is formed based on this by setting current density of the ion beam at the time of manufacture of a polycrystal thin film to 20-micrometerA/two or more cm, and making ion beam voltage fewer than more than 150V and 700V — the high oxide superconductivity of critical current density — a conductor can be obtained certainly In addition, the ion used as the aforementioned ion beam has an inactive gas ion or an inactive gas ion, and the mixed desirable ion of oxygen gas.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] the oxide superconductivity in which the manufacture method of a polycrystal thin film that crystal orientation was ready, as for this invention, and crystal orientation were ready — it is related with the manufacture method of a conductor

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Although the oxides superconductors become and discovered at recent years are outstanding superconductors which show the critical temperature exceeding liquid nitrogen temperature, in order to use this kind of oxides superconductors as a practical superconductor now, the trouble which should solve various exists. One of the trouble of the is the problem that the critical current density of oxides superconductors is low.
[0003] Although the problem that the critical current density of the aforementioned oxides superconductors is low is the cause with big an electric anisotropy existing in the crystal of oxides superconductors itself and especially oxides superconductors tend to pass the electrical and electric equipment to a shaft orientations and b shaft orientations of the crystallographic axis, it is known that it will be hard to pass the electrical and electric equipment to c shaft orientations. In order to form oxides superconductors on a base material from such a viewpoint and to use this as a superconductor, it is necessary to form the oxides superconductors of the good state of a crystal stacking tendency on a base material, to make the orientation of the a-axis or b-axis of the crystal of oxides superconductors carry out in the direction which is going to pass the electrical and electric equipment moreover, and to make the orientation of the c axis of oxides superconductors carry out in the direction of other.
[0004] Various meanses have been tried in order to form the good oxide superconductivity layer of a crystal stacking tendency on base materials, such as a substrate metallurgy group tape, conventionally. As the one method, the method of forming an oxide superconductivity layer by the forming-membranes methods, such as sputtering, on these single crystal base materials is enforced using single crystal base materials, such as MgO to which oxides superconductors and the crystal structure were similar, or SrTiO3.
[0005] If the forming-membranes methods, such as sputtering, are performed using Above MgO or the single crystal base material of SrTiO3, in order that the crystal of an oxide superconductivity layer may carry out a crystal growth based on the crystal of a single crystal base material, it is possible to make the crystal stacking tendency good, and it is known that the oxide superconductivity layer formed on these single crystal base materials will demonstrate hundreds of thousands - about two millions A/cm critical current density high enough.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] Since an ion beam is irradiated at the angle of 50 - the 60 directions of slant in case the constituent particle begun to beat from the target by sputtering is made to deposit on a base material as explained above according to the manufacture method of the polycrystal thin film of this invention As a result of a constituent particle's being efficiently activable, the polycrystal thin film of 30 or less grain-boundary inclinations which also raised the a-axis stacking tendency and the b-axis stacking tendency to the membrane formation side of a base material in addition to the c axis stacking tendency can be obtained. Furthermore, a crystal stacking tendency can be prepared still better by making the degree of incident angle of an ion beam into 55 - 60 degrees, and the polycrystal thin film of the good crystal stacking tendency of less than 25 grain-boundary inclinations can be obtained. The aforementioned polycrystal thin film has a good stacking tendency within a field in the a-axis and b-axis of crystal grain which constitute a polycrystal thin film since the diffraction peak of the X diffraction which is made to rotate it and is acquired appears every 90 degrees, and since the appearance range of the peak turns into the range of 0 - 30 degrees, it is also clear that the grain-boundary inclination is 30 degrees.
[0067] Moreover, the polycrystal thin film of a good crystal stacking tendency can be certainly manufactured by setting current density of the ion beam at the time of manufacture of a polycrystal thin film to 20-micrometerA/two or more cm, and making ion beam voltage fewer than more than 150V and 700V. In addition, the ion used as an ion beam has an inactive gas ion or an inactive gas ion, and the mixed desirable ion of oxygen gas.
[0068] Next, according to the manufacture method of the oxides superconductors concerning this invention, the good polycrystal thin film of the above crystal stacking tendencies is formed with 50 - the 60 degrees of incident angle of an ion beam on a base material, and an oxide superconductivity layer is formed on it. The aforementioned polycrystal thin film has the good stacking tendency within a field of the crystal grain which constitutes a polycrystal thin film since the diffraction peak of the X diffraction which is made to rotate it and is acquired appears every 90 degrees, and since it generates an oxide superconductivity layer on it, it can form the good oxide superconductivity layer of a crystal stacking tendency. therefore — since the sense of the a-axes of the crystal grain of an oxide superconductivity layer or b-axes can also be arranged — the high oxide superconductivity of critical current density — a conductor can be obtained furthermore, the oxide superconductivity which was further excellent in the crystal stacking tendency since the crystal stacking tendency could be prepared still better by making the degree of incident angle of an ion beam into 55 - 60 degrees and the polycrystal thin film of the good crystal stacking tendency of less than 25 grain-boundary inclinations was obtained — a conductor can be obtained
[0069] moreover, the thing for which the polycrystal thin film of a good crystal stacking tendency can be manufactured certainly, and an oxide superconductivity layer is formed based on this by setting current density of the ion beam at the time of manufacture of a polycrystal thin film to 20-micrometerA/two or more cm, and making ion beam voltage fewer than more than 150V and 700V — the high oxide superconductivity of critical current density — a conductor can be obtained certainly In addition, the ion used as the aforementioned ion beam has an inactive gas

ion or an inactive gas ion, and the mixed desirable ion of oxygen gas.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] By the way, in order to use oxides superconductors as a conductor, it is necessary to form the good oxide superconductivity layer of a crystal stacking tendency on the base material of long pictures, such as the shape of a tape. However, as for the metal tape itself, if an oxide superconductivity layer is directly formed on base materials, such as a metal tape, since it differs from oxides superconductors greatly, the crystal structure cannot form the good oxide superconductivity layer of a crystal stacking tendency at all by the polycrystalline substance, either. And a diffusion reaction arises between a metal tape and an oxide superconductivity layer with heat treatment performed in case an oxide superconductivity layer is formed, the crystal structure of an oxide superconductivity layer collapses, and there is a problem on which a superconductivity property deteriorates.
[0007] Then, using a sputtering system, covering interlayers, such as MgO and SrTiO3, and forming an oxide superconductivity layer on this interlayer on base materials, such as a metal tape, conventionally, is performed. However, the oxide superconductivity layer formed by the sputtering system on this kind of interlayer had the problem that only low critical current density (for example, thousands - about two 10,000 A/cm) was considerably shown rather than the oxide superconductivity layer formed on the single crystal base material. This is considered to be based on the reason for explaining below.
[0008] the oxide superconductivity which drawing 9 formed the interlayer 2 by the sputtering system on the base materials 1, such as a metal tape, and formed the oxide superconductivity layer 3 by the sputtering system on this interlayer 2 -- the cross-section structure of a conductor is shown In the structure shown in drawing 9 , the oxide superconductivity layer 3 is in a polycrystal state, and is in the state where much crystal grain 4 joined together disorderly. If each of such crystal grain 4 is seen separately, although orientation of the c axis of the crystal of each crystal grain 4 is perpendicularly carried out to the base-material front face, an a-axis and a b-axis will be considered to have turned to the disorderly direction.
[0009] Thus, if the sense of an a-axis and a b-axis becomes disorderly for every crystal grain of an oxide superconductivity layer, as a result of [**** in the quantum unity of a superconductivity state] being divided, in the grain boundary to which the crystal stacking tendency was confused, it will be thought that the fall of a superconductivity property, especially critical current density is caused. Moreover, it is thought that the aforementioned oxides superconductors will be in an a-axis and the polycrystal state which has not carried out b-axis orientation for the oxide superconductivity layer 3 growing so that it may have consistency into an interlayer's 2 crystal when forming the oxide superconductivity layer 3, since the interlayer 2 formed in the bottom of it is in an a-axis and the polycrystal state which has not carried out b-axis orientation.
[0010] By the way, the technology which forms various kinds of orientation films on the base material of the polycrystalline substance in addition to the applicable field of the aforementioned oxides superconductors is used. for example, although it is fields, such as a field of an optical thin film, a field of a magneto-optic disk, a field of a wiring substrate, a RF waveguide, and a high pass filter, a cavity resonator, also in which technology, the good polycrystal thin film of the stacking tendency by which membraneous quality was stabilized is formed on a base material --

things have been technical problems That is, if quality, such as an optical thin film which will be formed on it if the crystal stacking tendency of a polycrystal thin film is good, a magnetic thin film, and a thin film for wiring, improves and the direct formation of the good optical thin film of a crystal stacking tendency, a magnetic thin film, the thin film for wiring, etc. can be further carried out on a base material, in addition, it will be desirable.

[0011] Moreover, as core material of the magnetic head used in a high-frequency band, it has high permeability and, also thermally, magnetic thin films, such as a stable permalloy or a Sendust, are put in practical use. Although these magnetic thin films were conventionally formed on the predetermined substrate of vacuum evaporationo or the spatter, control of the magnetic anisotropy of a magnetic thin film became it difficult that the stacking tendency of the crystal orientation of these magnetic thin films was a low thing, within the film surface, the direction of crystal grain became disorderly and they had the problem by which the RF property of permeability is spoiled. Moreover, the local fluctuation called a skew and ripple to the magnetization within a field as the shaft orientations of the crystallographic axis within a film surface are disorderly will occur, and the RF property of permeability will be spoiled as mentioned above.

[0012] the oxide superconductivity equipped with offering the polycrystal thin film which could also arrange the a-axis and the b-axis of a crystallographic axis of crystal grain along the field parallel to a membrane-formation side, and was excellent in the crystal stacking tendency, while it was made in order that this invention might solve the aforementioned technical problem, and orientation of the c axis of a crystallographic axis can be carried out to the right-angle sense to the membrane-formation side of a base material, and the oxide-superconductivity layer excellent in the crystal stacking tendency — it aims at offering a conductor

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[Translation done.]

MEANS

[Means for Solving the Problem] In the method of beginning to beat the constituent particle of a target by sputtering, making deposit on a base material, and forming a polycrystal thin film on a base material, in order that invention according to claim 1 may solve the aforementioned technical problem The aforementioned constituent particle is made to deposit on a base material, irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material with the degree of incident angle of the range of 50 – 60 degrees, in case the aforementioned constituent particle is made to deposit on a base material.
[0014] In the method of beginning to beat the constituent particle of a target by sputtering, making deposit on a base material, and forming a polycrystal thin film on a base material, in order that invention according to claim 2 may solve the aforementioned technical problem While making the aforementioned constituent particle deposit on a base material, irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material in case the aforementioned constituent particle is made to deposit on a base material Current density of the aforementioned ion beam is made into two or more 20microA/cm, and ion beam voltage is made into less than [700V] or more by 150.
[0015] Invention according to claim 3 makes the grain-boundary inclination of the crystal grain of the polycrystal thin film which sets the degree of incident angle of an ion beam as the range of 55 – 60 degrees, and is formed on a base material less than 25 degrees in the manufacture method of a polycrystal thin film according to claim 1, in order to solve the aforementioned technical problem.
[0016] Invention according to claim 4 uses an inactive gas ion or the mixed ion of inert gas and oxygen gas as ion according to claim 1 or 2, in order to solve the aforementioned technical problem.
[0017] In order to solve the aforementioned technical problem, invention according to claim 5 begins to beat the constituent particle of a target by sputtering, and is made to deposit it on a base material. In the manufacture method of a conductor the oxide superconductivity which forms a polycrystal thin film on a base material, and forms an oxide superconductivity layer subsequently to this polycrystal thin film top — Irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material with the degree of incident angle of the range of 50 – 60 degrees, in case the aforementioned constituent particle is made to deposit on a base material, make a spatter particle deposit and a polycrystal thin film is formed. An oxide superconductivity layer is formed on this polycrystal thin film.
[0018] In order to solve the aforementioned technical problem, invention according to claim 6 begins to beat the constituent particle of a target by sputtering, and is made to deposit it on a base material. In the manufacture method of a conductor the oxide superconductivity which forms a polycrystal thin film on a base material, and forms an oxide superconductivity layer subsequently to this polycrystal thin film top — While making a spatter particle deposit, irradiating the ion beam which the ion source generated from across to the membrane formation side of a base material in case the aforementioned constituent particle is made to deposit on a base material Two or more 20microA/cm are formed for the current density of the aforementioned ion beam, a polycrystal thin film is formed for ion beam voltage as less than

[700V.] or more by 150, and an oxide superconductivity layer is formed on this polycrystal thin film.
[0019] in order that invention according to claim 7 may solve the aforementioned technical problem -- oxide superconductivity according to claim 5 or 6 -- in the manufacture method of a conductor, the grain-boundary inclination of the crystal grain of the polycrystal thin film which sets the degree of incident angle of an ion beam as the range of 55 - 60 degrees, and is formed on a base material is made into less than 25 degrees
[0020] Invention according to claim 8 is the manufacture method of the oxides superconductors characterized by growing the crystal of oxides superconductors epitaxially to the crystal of a polycrystal thin film in case an oxide superconductivity layer is formed on a polycrystal thin film according to claim 5, 6, or 7, in order to solve the aforementioned technical problem.
[0021] Invention according to claim 9 is the manufacture method of the oxides superconductors according to claim 5, 6, 7, or 8 characterized by using an inactive gas ion or the mixed ion of inert gas and oxygen gas as ion in order to solve the aforementioned technical problem.

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

OPERATION

[Function] As a result of activating a constituent particle efficiently since an ion beam is also simultaneously irradiated from the range of the 50 - 60 directions of slant of a base material in case the spatter particle begun to beat from the target by sputtering is made to deposit on a base material, in addition to a c axis stacking tendency, an a-axis stacking tendency and a b-axis stacking tendency also improve to the membrane formation side of a base material. consequently — even if it is the polycrystal thin film in which much grain boundaries were formed — both the a-axis stacking tendency for every crystal grain a b-axis stacking tendency and a c axis stacking tendency — although — it becomes good and the polycrystal thin film which improved is obtained Moreover, in order to activate the constituent particle in the case of a spatter, the mixed ion of argon ion or argon ion, and oxygen ion is desirable.
[0023] In addition, this inventions assume the following things as a factor in which the crystal stacking tendency of the aforementioned polycrystal thin film is ready. In the unit lattice of the crystal of the cubic polycrystal thin film formed on the substrate, the directions of a substrate normal are <100> shafts, and each of other <010> shafts and <001> shafts serves as a direction which intersects perpendicularly with <100> shafts. If the ion beam which carries out incidence from across to a substrate normal is taken into consideration to these directions, when carrying out incidence along the direction of the diagonal line of a unit lattice, i.e., <111> shafts, to the zero of a unit lattice, it becomes the 54.7 degrees of incident angle. A good crystal stacking tendency is shown here in the range whose degree of incident angle of an ion beam is 50 - 60 degrees as mentioned above, The degree of incident angle of an ion beam is considered that the bird clapper is related before and after it in accordance with the 54.7 aforementioned degrees. In the crystal which ion channeling took place most effectively when these angles were in agreement or having been approximated, and has been deposited on a base material Only the atom which became the arrangement relation which is in agreement with the aforementioned angle on the upper surface of a base material becomes easy to remain alternatively. As a result of a spatter's being carried out by the spatter effect which the ion beam by which incidence is carried out aslant generates and being removed, only the crystal into which the good atoms of a stacking tendency gathered remained alternatively, and deposited the thing of the atomic arrangement to which others were confused, this became a cause and it presumes that in which a crystal stacking tendency is ready.
[0024] Therefore, if too low, it will become the shortage of ion irradiation, the aforementioned effect is made hard to produce, and when ion beam voltage is too high, it will produce the spatter effect conversely and will disturb a crystal stacking tendency. As for the current density of the above thing to an ion beam, it is desirable to consider as two or more 20microA/cm, and, as for ion beam voltage, it is desirable to consider as less than [700V] more than by 150V.
[0025] Moreover, if an oxide superconductivity layer is grown epitaxially on the good polycrystal thin film of the aforementioned crystal stacking tendency, as a result of an oxide superconductivity layer's carrying out a crystal growth along with the crystal of a polycrystal thin film, what has an a-axis stacking tendency, a b-axis stacking tendency, and a c axis stacking tendency good [an oxide superconductivity layer] is obtained.

[Translation done.]

EXAMPLE

[Example] Hereafter, the example of this invention is explained with reference to a drawing. The polycrystal thin film by which A was formed in the base material of a tabular and B was formed [in / drawing 1 / drawing 1 shows one example in which the polycrystal thin film of this invention was formed on the base material, and] in the upper surface of a base material A is shown. The aforementioned base material A can use the thing of various configurations, such as a plate, a wire rod, and tape material, and a base material A consists of metallic materials, such as silver, platinum, stainless steel, and copper, an alloy, various glass or various ceramics, etc.
[0027] It comes to carry out junction unification through the grain boundary, and the c axis of the crystallographic axis of each crystal grain 20 is turned right-angled to the upper surface (membrane formation side) of a base material A, the a-axes and b-axes of a crystallographic axis of each crystal grain 20 are mutually turned in the same direction, and orientation within a field of much detailed crystal grain 20 in which the aforementioned polycrystal thin film B has the crystal structure of cubic system is carried out mutually. Moreover, orientation of the c axis of each crystal grain 20 is carried out right-angled to the membrane formation (upper surface) side of a base material A. And the a-axes (or b-axis) of each crystal grain 20 make those angles (the grain-boundary inclination K shown in drawing 2) to make less than 30 degrees, and junction unification is carried out.
[0028] Next, the equipment which manufactures the aforementioned polycrystal thin film B is explained. Drawing 3 shows an example of equipment which manufactures the aforementioned polycrystal thin film B, and the equipment of this example has the composition of having prepared the ion gun for ion beam assistance in the sputtering system.
[0029] The target 12 of a tabular with which opposite arrangement of the equipment of this example was carried out with the predetermined interval in the slanting upper part of the base-material electrode holder 11 which holds a base material A horizontally, and this base-material electrode holder 11, The spatter beam irradiation equipment 14 which the slanting upper part of the aforementioned base-material electrode holder 11 was countered with the predetermined interval, and the ion gun 13 which estranged with the target 12 and has been arranged, and the aforementioned target 12 set caudad, and has been arranged towards the inferior surface of tongue of a target 12 is constituted as a subject. Moreover, the sign 15 in drawing shows the target electrode holder holding the target 12.
[0030] Moreover, the equipment of this example is contained by the vacuum housing of illustration abbreviation, and can hold the circumference of a base material A now in vacuum atmosphere. Furthermore, controlled-atmosphere sources of supply, such as a chemical cylinder, are connected to the aforementioned vacuum housing, and it can be made the inert gas atmosphere which is in low voltage states, such as a vacuum, about the interior of a vacuum housing, and contains the inert gas atmosphere or oxygen of argon gas or others now.
[0031] In addition, when using a long metal tape (tapes, such as a product made from a Hastelloy, or a product made from stainless steel) as a base material A, it is desirable to constitute so that continuation membrane formation of the polycrystal thin film can be carried out on a tape-like base material by forming the sending-out equipment and take-up motion of a metal tape in the interior of a vacuum housing, and sending out a base material A and rolling

round to the base-material electrode holder 11 with take-up motion continuously from sending-out equipment. The aforementioned base-material electrode holder 11 equips the interior with a heating heater, and can heat now the base material A located on the base-material electrode holder 11 to the temperature of business. Moreover, the angle adjustment mechanism D is attached to the pars basilaris ossis occipitalis of the base-material electrode holder 11. This angle adjustment mechanism D is constituted considering the pedestal 7 which supports the up support plate 5 joined to the pars basilaris ossis occipitalis of the base-material electrode holder 11, the lower support plate 6 by which pin combination was carried out at this up support plate 5, and this lower support plate 6 as a subject. The aforementioned up support plate 5 and the lower support plate 6 are mutually constituted free [rotation] through a part for a pin bond part, and can adjust now the level angle of the base-material electrode holder 11. In addition, although the angle adjustment mechanism D in which the angle of the base-material electrode holder 11 was adjusted was established in this example, the angle adjustment mechanism D is attached in the ion gun 13, the degree of tilt angle of the ion gun 13 is adjusted, and you may make it adjust the degree of incident angle of an ion beam. Moreover, an angle adjustment mechanism cannot be restricted to the composition of this example, and, of course, the thing of various composition can be adopted.

[0032] The aforementioned target 12 is for forming the polycrystal thin film made into the purpose, and the thing of the same composition as the polycrystal thin film of the target composition or approximation composition etc. is used for it. What is necessary is not to restrict to this, although the zirconia (YSZ) specifically stabilized by MgO or Y2O3, MgO, SrTiO3, etc. are used as a target 12, and just to use TAGETSU corresponding to the polycrystal thin film which it is going to form.

[0033] Inside the container, the aforementioned ion gun 13 contains an evaporation source, pulls it out near the evaporation source, is equipped with an electrode and constituted. And it is equipment which it controls by the electric field which ionized a part of atom generated from the aforementioned evaporation source, or molecule, pulled out the ionized particle, and were generated in the electrode, and is irradiated as an ion beam. There are various things, such as a direct-current-discharge method, a RF excitation method, a filament formula, and a cluster ion beam method, in ionizing a particle. A filament formula is the method of carrying out energization heating at the filament made from a tungsten, making generate a thermoelectron, making collide with an evaporation particle in a high vacuum, and ionizing. Moreover, from the nozzle prepared in opening of the crucible to which the raw material was paid, by the thermoelectron, a cluster ion beam method carries out the shock of the cluster of the set molecule which comes out in a vacuum, ionizes it, and emits it. In this example, the ion gun 13 of the internal structure of composition of being shown in drawing 4 (a) is used. This ion gun 13 is constituted in preparation for the interior of the tubed container 16 in the drawer electrode 17, a filament 18, and the introductory pipes 19, such as Ar gas, and can irradiate ion in parallel with the shape of a beam from the nose of cam of a container 16.

[0034] As shown in drawing 3 , the aforementioned ion gun 13 has the medial axis S, made it incline to the upper surface (membrane formation side) of a base material A with the degree theta of incident angle (angle of the perpendicular (normal) of a base material A, and a center line S to make), and has countered. Although this degree theta of incident angle has the desirable range of 50 - 60 degrees, the range of 55 - 60 degrees is the most desirable. Therefore, the ion gun 13 is arranged so that it may have with a tilt angle theta to the upper surface of a base material A and the incidence of the ion beam can be carried out. In addition, the ion beam which irradiates a base material A according to the aforementioned ion gun 13 is good at the ion beam of rare gas, such as helium+, Ne+, Ar+, Xe+, and Kr+, or the mixed ion beam of them and oxygen ion. in order to prepare the crystal structure of a polycrystal thin film, a certain amount of atomic weight is required, and when it takes into consideration that it is thin ineffective with too much lightweight ion, it is desirable [it is **, and] to use ion, such as Ar+ and Kr+

[0035] The aforementioned spatter beam irradiation equipment 14 irradiates an ion beam in composition equivalent to the ion gun 13 to nothing and a target 12, and can begin to beat the

constituent particle of a target 12. In addition, with this invention equipment, since it is important that the constituent particle of a target 13 can be begun to beat, the seal of approval of the voltage is carried out to a target 12 by the high frequency coil etc., the constituent particle of a target 12 may be begun to beat, and it may constitute so that it may be possible, and the spatter beam irradiation equipment 14 may be omitted.
[0036] Next, the case where the polycrystal thin film B of YSZ is formed on a base material A using the equipment of the aforementioned composition is explained. In order to form the polycrystal thin film B on a base material A, while using the target of YSZ, it enables it to irradiate the ion beam which the angle adjustment mechanism D is adjusted and is irradiated from the ion gun 13 at an angle of the range of 50 - 60 degrees on the upper surface of the base-material electrode holder 11. Next, vacuum length of the interior of the container which has contained the base material A is carried out, and it considers as reduced pressure atmosphere. And the ion gun 13 and the spatter beam irradiation equipment 14 are operated.
[0037] If an ion beam is irradiated from the spatter beam irradiation equipment 14 at a target 12, the constituent particle of a target 12 will be begun to beat, and it will come flying on a base material A. And the mixed ion beam of Ar ion and oxygen ion is irradiated from the ion gun 13 at the same time it makes the constituent particle begun to beat from the target 12 deposit on a base material A. The degree theta of incident angle at this time of carrying out ion irradiation has 50 - 60 most desirable degrees. If theta is made into 90 degrees here, although orientation of the c axis of a polycrystal thin film is carried out right-angled to the membrane formation side of a base material A, since a field (111) stands on the membrane formation side of a base material A, it is not desirable. Moreover, if theta is made into 30 degrees, a polycrystal thin film will not carry out even c axis orientation. If ion beam irradiation is carried out at an angle of the above desirable ranges, the field (100) of the crystal of a polycrystal thin film will come to stand.
[0038] Although orientation of the a-axis and b-axis of a crystallographic axis of YSZ which are formed on a base material A can be carried out by performing sputtering, performing ion beam irradiation with such a degree of incident angle, it is thought that this is based on the result efficiently activated by having carried out ion beam irradiation at the suitable angle to the spatter particle in the middle of having deposited. [of a polycrystal thin film]
[0039] In addition, this inventions assume the following things as a factor in which the crystal stacking tendency of this polycrystal thin film B is ready. The unit lattice of the crystal of the polycrystal thin film B of YSZ is a cubic as shown in drawing 4 (b), in this crystal lattice, the directions of a substrate normal are <100> shafts, and each of other <010> shafts and <001> shafts serves as a direction shown in drawing 4 (b). If the ion beam which carries out incidence from across to a substrate normal is taken into consideration to these directions, when carrying out incidence along the direction of the diagonal line of a unit lattice, i.e., <111> shafts, to the zero O of drawing 4 (b), it becomes the 54.7 degrees of incident angle. That a good crystal stacking tendency is shown in the range of the 50 - 60 degrees of incident angle as mentioned above here In the crystal which ion channeling took place most effectively and has deposited on a base material A when the degree of incident angle of an ion beam comes before and after it in accordance with the 54.7 aforementioned degrees Only the atom which became the arrangement relation which is in agreement with the aforementioned angle on the upper surface of a base material A becomes easy to remain alternatively. The thing of the atomic arrangement to which others were confused presumes what only the crystal into which the good atoms of a stacking tendency gathered remains alternatively, and deposits, as a result of a spatter's being carried out by the spatter effect of an ion beam and being removed.
[0040] The aforementioned effect is made hard to become the shortage of ion irradiation and to produce from the above thing, if the ion beam voltage at the time of irradiating an ion beam is too low, and when too high, conversely, the spatter effect becomes high and will disturb a crystal stacking tendency. As for the current density of the above thing to an ion beam, it is desirable to consider as two or more 20microA/cm, and, as for ion beam voltage, it is desirable to consider as less than [700V] more than by 150V.
[0041] The base material A which the polycrystal thin film B of YSZ deposited on drawing 1 and drawing 2 by the aforementioned method is shown. In addition, although drawing 1 shows the

state where one layer of crystal grain 20 was formed, of course, it does not interfere by the multilayer structure of crystal grain 20.
[0042] next, the oxide superconductivity which drawing 5 and drawing 6 require for this invention — what shows one example of a conductor — it is — the oxide superconductivity of this example — the conductor 23 consists of an oxide superconductivity layer C formed in the upper surface of the polycrystal thin film B formed in the upper surface of the base material A of a tabular, and this base material A, and the polycrystal thin film B The aforementioned base material A and the polycrystal thin film B consist of material equivalent to the material explained in the previous example, and crystal orientation of the crystal grain 20 of the polycrystal thin film B is carried out so that it may become less than 30 grain-boundary inclinations, as shown in drawing 1 and drawing 2 .
[0043] Next, the oxide superconductivity layer C is covered by the upper surface of the polycrystal thin film B, orientation of the c axis of the crystal grain 23 is carried out right-angled to the upper surface of the polycrystal thin film B, orientation within a field is carried out along a field parallel to the base-material upper surface like the polycrystal thin film B of the crystal grain 23 — which explained the a-axis and the b-axis previously, and grain-boundary inclination K' which crystal grain 23 form is made into less than 30 degrees. The oxides superconductors which constitute this oxide superconductivity layer Composition Y1Ba2Cu3Ox, Y2Ba4Cu8Ox, and Y3Ba3Cu6Ox — Or (Bi, Pb) 2calcium2Sr2Cu3Ox, composition which becomes 4 Ox 3 Cu 2 Sr 2 (Bi, Pb) calcium, or Tl2Ba2calcium2Cu3Ox, Tl1Ba2calcium2Cu3Ox, and Tl1Ba2calcium3Cu4Ox — they are oxides superconductors with the high critical temperature represented by composition etc.
[0044] Next, the equipment which forms the oxide superconductivity layer C is explained. Drawing 7 shows an example of the equipment which forms an oxide superconductivity layer by the forming-membranes method, and drawing 7 shows laser vacuum evaporationo equipment. The laser vacuum evaporationo equipment 30 of this example has the processing container 31, and can install now a base material A and a target 33 in the vacuum evaporationo processing room 32 inside this processing container 31. That is, while a pedestal 34 is formed in the bottom of the vacuum evaporationo processing room 32 and being able to install a base material A in the upper surface of this pedestal 34 in the level state, the target 33 supported by the support electrode holder 36 is formed in the slanting upper part of a pedestal 34 in the state of the inclination. It connects with the evacuation equipment of illustration abbreviation through an exhaust hole 37, and the processing container 31 can decompress the interior now to a predetermined pressure.
[0045] The aforementioned target 33 consists of boards, such as a sintered compact of equivalent to the oxide superconductivity layer C which it is going to form, or the multiple oxide which made much approximated composition or many components which are easy to flee during membrane formation contain, or oxides superconductors. The aforementioned pedestal 34 is what built in the heating heater, and can heat a base material A now to desired temperature.
[0046] Laser luminescence equipment 38, the 1st reflecting mirror 39, a condenser lens 40, and the 2nd reflecting mirror 41 are formed in the side of the processing container 31, and it has come to be, able to carry out the convergent radiotherapy of the laser beam which laser luminescence equipment 38 generated to a target 33 on the other hand through the transparent aperture 42 in which it was attached by the side attachment wall of the processing container 31. As long as laser luminescence equipment 38 can begin to beat a constituent particle from a target 33, it may use which things, such as an YAG laser, a CO2 laser, and an excimer laser.
[0047] Next, the case where the oxide superconductivity layer C is formed on the polycrystal thin film B of Above YSZ is explained. If the polycrystal thin film B of YSZ is formed on a base material A as mentioned above, an oxide superconductivity layer will be formed on this polycrystal thin film B. When forming an oxide superconductivity layer on the polycrystal thin film B, in this example, the laser vacuum evaporationo equipment 30 shown in drawing 7 is used.
[0048] It installs on the pedestal 34 of the laser vacuum evaporationo equipment 30 which shows the base material A in which the polycrystal thin film B was formed to drawing 7 , and the vacuum evaporationo processing room 32 is decompressed with a vacuum pump. Oxygen gas is

introduced into the vacuum evaporationo processing room 32 here if needed, and it is good also considering the vacuum evaporationo processing room 32 as an oxygen atmosphere. Moreover, the heating heater of a pedestal 34 is operated and a base material A is heated to desired temperature.

[0049] Next, the convergent radiotherapy of the laser beam which made it generate from laser luminescence equipment 38 is carried out to the target 33 of the vacuum evaporationo processing room 32. By this, whether the constituent particle of a target 33 begin to be scooped out evaporates, and the particle deposits on the polycrystal thin film B. Since the polycrystal thin film B carries out c axis orientation beforehand and is carrying out orientation also of an a-axis and the b-axis in the case of deposition here of a constituent particle, it grows epitaxially and crystallizes so that the c axis, a-axis, and b-axis of the crystal of the oxide superconductivity layer C which are formed on the polycrystal thin film B may also be adjusted in the polycrystal thin film B. The good oxide superconductivity layer C of a crystal stacking tendency is obtained by this.

[0050] Although the oxide superconductivity layer C formed on the aforementioned polycrystal thin film B will be in a polycrystal state, in each of the crystal grain of this oxide superconductivity layer C, as shown in drawing 6 , the c axis which cannot pass the electrical and electric equipment easily in the thickness direction of a base material A carries out orientation of it, and a-axes or b-axes are carrying out orientation to the longitudinal direction of a base material A. Therefore, the obtained oxide superconductivity layer is excellent in the quantum unity in the grain boundary, since there is little degradation of the superconductivity property in the grain boundary, it is easy to pass the electrical and electric equipment in the direction of a field of a base material A, and what was excellent in critical current density is obtained.

[0051] On the other hand, drawing 8 shows other examples of the equipment for manufacturing a polycrystal thin film. The same sign is given to a component equivalent to the equipment indicated to drawing 3 in the equipment of this example, and those explanation is omitted. Differing from the equipment shown in drawing 3 in the equipment of this example is the point of having formed three targets 12, having formed three spatter beam irradiation equipments 14, and having connected RF generator 29 to the base material A and the target 12.

[0052] With the equipment of this example, since begin to beat the particle of another kind, respectively, it is made to deposit on a base material A and a bipolar membrane can be formed from three targets 12, 12, and 12, there is the feature which can also manufacture the polycrystal film of more complicated composition. Moreover, RF generator 30 can be operated and a spatter can also be carried out from a target 12. When enforcing the aforementioned method using the equipment of this example, the polycrystal thin film which was excellent in the stacking tendency like the case of the equipment shown in drawing 3 can be obtained.

[0053] (Example of manufacture) The equipment of composition of being shown in drawing 3 was used, vacuum length of the interior of a container which contained this equipment was carried out with the vacuum pump, and it decompressed to 3.0x10 to 4 torrs. The base material used Hastelloy C276 tape with 0.5mm [in width of face of 10mm, and thickness], and a length of 10cm. The target set the degree of incident angle of the beam of spatter voltage 1000V, 100mA of spatter current, and the ion source as 55 degrees using the thing made from YSZ (stabilized zirconia), the assistant voltage of the ion source was set as 300V, the current density of an ion beam was set as 10-70microA/cm2, respectively, on the base material, ion irradiation was performed simultaneously with sputtering and the YSZ layer of the shape of a film with a thickness of 0.3 micrometers was formed. The current density of the aforementioned ion beam is based on the count value of the current density metering device grounded near the sample here.

[0054] The X diffraction examination by the theta-2theta method for having used CuK alpha rays about each obtained polycrystal thin film sample of YSZ was performed. Drawing 10 - drawing 13 are drawings showing 55 incident angles of the ion source, and the diffraction strength of the sample which measured the current density of an ion beam by ion beam voltage 300V, respectively to 10microA/cm2, 20microA/cm2, 40microA/cm2, and 70microA/cm2. From the

result shown in drawing 10 - drawing 13 , the current density of an ion beam by the sample set as 20-70microA/cm2 The peak of the field (200) of YSZ or (400) a field is accepted, and that in which the field (100) of the polycrystal thin film of YSZ is carrying out orientation along the field parallel to a base-material front face can be presumed. It became clear that the polycrystal thin film of YSZ carries out orientation of the C shaft at right angles to the base-material upper surface, and is formed. In addition, the peak of YSZ is not seen if it is in the sample which made ion beam current density 10microA/cm2 from the result shown in drawing 10 . Therefore, when ion beam current density was too low, it became clear that control of the crystal stacking tendency of a polycrystal thin film cannot be performed.
[0055] Then, drawing 14 - drawing 17 show the pole figure in each aforementioned sample. By the sample which made current density of an ion beam 10microA/cm2, a c axis stacking tendency was not seen but the result shown in drawing 10 - drawing 13 and the equivalent result were obtained so that clearly from these drawings. It became clear that the current density at the time of irradiating an ion beam from the above thing is two or more 20microA/cm need.
[0056] Drawing 18 - drawing 20 are drawings showing the diffraction strength of the sample which changed ion beam voltage and ion beam current suitably, and measured them with the 90 degrees of incident angle of the ion source. The beam current shown in each drawing here shows the current for loads of the ion gun used for the experiment. From the result shown in drawing 18 - drawing 20 , even if it set the degree of incident angle of the ion source as 90 degrees, the peak (200) and peak (400) of YSZ could be accepted, and sufficient stacking tendency was accepted about the c axis stacking tendency.
[0057] Next, in each sample by which c axis orientation was carried out as mentioned above, it measured whether the a-axis or b-axis of a YSZ polycrystal thin film would carry out orientation. For the measurement, as shown in drawing 21 , while irradiating an X-ray at an angle theta at the polycrystal thin film of YSZ formed on the base material A In the vertical plane containing an incidence X-ray, install the X-ray counter 25 in the position of the angle of 2theta (58.7 degrees) to an incidence X-ray, and the value of the level angle phi to the vertical plane containing an incidence X-ray is changed suitably. That is, the stacking tendency of the a-axes of the polycrystal thin film B or b-axes was measured by measuring the diffraction strength obtained when only an angle of rotation phi makes it rotate as a base material A is shown in an arrow in drawing 21 . The result is shown in drawing 22 and drawing 23 .
[0058] When a diffraction peak does not appear in the case of the sample which set the degree of incident angle of an ion beam as 55 degrees, and manufactured it as shown in drawing 22 , but phi is made into 90 degrees and 0 times, the peak of the field (311) of YSZ has appeared every 90 degrees to the angle of rotation phi. This is equivalent to the peak (011) of YSZ within a substrate side, and it became clear that the a-axes or b-axes of a YSZ polycrystal thin film is carrying out orientation. On the other hand, as shown in drawing 23 , in the case of the sample which set the degree of ion beam incident angle as 90 degrees, and manufactured it, a special peak was not seen but that it is disorderly made an a-axis and b shaft orientation clear.
[0059] It became clear that the polycrystal thin film of the sample manufactured by the aforementioned equipment from the above result is carrying out orientation of a-axes and the b-axes as well as c axis orientation. Therefore, it became clear that polycrystal thin films, such as YSZ excellent in the stacking tendency, can be manufactured.
[0060] On the other hand, drawing 24 shows the result which examined the crystal stacking tendency in each crystal grain of the polycrystal layer of this sample using the sample of a YSZ polycrystal thin film used by drawing 22 . In this examination, when performing an X diffraction by the method previously explained based on drawing 21 , the diffraction peak at the time of setting the angle of phi as the value of serration 5 times to -ten - 45 degrees is measured. Although the diffraction peak of the polycrystal thin film of YSZ obtained from the result shown in drawing 24 appears in less than 30 grain-boundary inclinations, its having disappeared is clear at 45 degrees. Therefore, having fitted in less than 30 degrees made clear the grain-boundary inclination of the crystal grain of the obtained polycrystal thin film, and it became clear to have a good stacking tendency.
[0061] Next, ion beam voltage was set as each value of 500V, 700V, 200V, and 150V on

conditions almost equivalent to the aforementioned manufacture conditions, and the X diffraction examination was performed about the sample which set the current density of an ion beam as each value of 40microA/cm2, 50microA/cm2, 20microA/cm2, and 30microA/cm2, and manufactured it. Those results are shown in drawing 25 – drawing 29 .

[0062] Moreover, the relation of the above ion beam voltage and ion beam current density which were obtained from the test result shown in drawing 25 – drawing 29 , and the relevance of the crystal stacking tendency of a polycrystal thin film are shown in drawing 30 . From the result shown in drawing 30 , even if each of ion beam voltage and ion beam current density is too high and it is too low, it is unsuitable, it is more than 150V, and ion beam voltage needs to be fewer than 700V, and it became clear that the current density of an ion beam is required for two or more 20microA/cm.

[0063] Next, the current density of 300V and an ion beam is set as 40microA/cm2, ion beam energy is set as 300eV for ion beam voltage, and when the degree of incident angle of an ion beam is changed to zero – 65 degrees and a polycrystal thin film is manufactured, the relation between the degree of incident angle in the distribution of the direction (111) of the crystal of the obtained polycrystal thin film and full width at half maximum is shown. In addition, all the aforementioned half-the-price values asked for the pole figure as shown in drawing 16 about each obtained sample, and when the auxiliary wires e and f as shown in drawing 16 from the center of this pole figure were drawn, they asked for it, the half angle, i.e., the peak ratio half, of the angle alpha which these auxiliary wires e and f make. The bird clapper became [the crystal stacking tendency] clear good in the range whose degree of incident angle of the result shown in drawing 31 to an ion beam is 50 – 60 degrees. Moreover, it also became clear by making the degree of incident angle of an ion beam into 55 – 60 degrees especially that a grain-boundary inclination is made to the minimal value of about 25 degrees.

[0064] Next, the oxide superconductivity layer was formed using the laser vacuum evaporationo equipment of composition of being shown in drawing 7 on the aforementioned polycrystal thin film. as a target — Y0.7Ba1.7Cu 3.0O7-x — the target which consists of oxides superconductors of composition was used Moreover, the interior of a vacuum evaporationo processing room was decompressed to 10 to 6 torrs, and laser vacuum evaporationo was performed at the room temperature. ArF laser with a wavelength of 193nm was used as laser for target evaporation. Then, it heat-treated in 60 minutes and in oxygen atmosphere by 400 degreeC. The obtained oxides superconductors are things with a width of face [of 0.5mm], and a length of 10cm.

[0065] this oxide superconductivity — the result which cooled the conductor and performed measurement of critical temperature and critical current density — critical temperature =90K Critical-current-density =500000 A/cm2 was shown, and it has checked demonstrating a very excellent superconductivity property.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing 1 is the block diagram showing the polycrystal thin film formed by this invention method.
[Drawing 2] Drawing 2 is the expansion plan showing the crystal grain, its crystal orientation, and grain-boundary inclination of the polycrystal thin film shown in drawing 1 .
[Drawing 3] Drawing 3 is the block diagram showing an example of equipment which enforces this invention method and manufactures a polycrystal thin film on a base material.
[Drawing 4] Drawing 4 is the cross section showing an example of the ion source of the equipment shown in drawing 3 .
[Drawing 5] Drawing 5 is the block diagram showing the oxide superconductivity layer formed on the polycrystal thin film shown in drawing 1 .
[Drawing 6] Drawing 6 is the expansion plan showing the crystal grain, its crystal orientation, and grain-boundary inclination of the oxide superconductivity layer shown in drawing 5 .
[Drawing 7] Drawing 7 is the block diagram showing an example of the equipment for forming an oxide superconductivity layer on a polycrystal thin film.
[Drawing 8] Drawing 8 is the block diagram showing other examples of this invention equipment.
[Drawing 9] Drawing 9 is the block diagram showing the polycrystal thin film manufactured with conventional equipment.
[Drawing 10] Drawing 10 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 300 current-density [V and ion beam] A/cm2 of 10micro.
[Drawing 11] Drawing 11 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 300 current-density [V and ion beam] A/cm2 of 20micro.
[Drawing 12] Drawing 12 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 300 current-density [V and ion beam] A/cm2 of 40micro.
[Drawing 13] Drawing 13 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 300 current-density [V and ion beam] A/cm2 of 70micro.
[Drawing 14] Drawing 14 is the pole figure of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 300 current-density [V and ion beam] A/cm2 of 10micro.
[Drawing 15] Drawing 15 is the pole figure of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 300 current-density [V and ion beam] A/cm2 of 20micro.
[Drawing 16] Drawing 16 is the pole figure of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 300 current-density [V and ion beam] A/cm2 of 40micro.
[Drawing 17] Drawing 17 is the pole figure of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 300 current-density [V and ion beam]

A/cm2 of 70micro.
[Drawing 18] Drawing 18 is a graph which shows the 90 degrees of ion beam incident angle, ion beam voltage 300V, 25mA of ion beam current, and the X diffraction result of the polycrystal thin film manufactured by 45mA.
[Drawing 19] Drawing 19 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 90 degrees of ion beam incident angle, ion beam voltage 500V, 15mA of ion beam current, 25mA, and 35mA.
[Drawing 20] Drawing 20 is a graph which shows the X diffraction result of the polycrystal thin film manufactured with the 90 degrees of ion beam incident angle, ion beam voltage 700V, and 25mA of ion beam current.
[Drawing 21] Drawing 21 is a block diagram for explaining the examination performed in order to investigate the a-axis and b-axis stacking tendency of a polycrystal thin film.
[Drawing 22] Drawing 22 is a graph which shows the diffraction peak of the field (311) of the manufactured polycrystal thin film.
[Drawing 23] Drawing 23 is a graph which shows the diffraction peak of the field (311) of the manufactured polycrystal thin film.
[Drawing 24] Drawing 24 is a graph which shows the diffraction peak for every five angle of rotation of the obtained polycrystal thin film.
[Drawing 25] Drawing 25 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 500 current-density [V and ion beam] A/cm2 of 40micro.
[Drawing 26] Drawing 25 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 700 current-density [V and ion beam] A/cm2 of 40micro.
[Drawing 27] Drawing 27 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 200 current-density [V and ion beam] A/cm2 of 50micro.
[Drawing 28] Drawing 28 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 200 current-density [V and ion beam] A/cm2 of 20micro.
[Drawing 29] Drawing 29 is a graph which shows the X diffraction result of the polycrystal thin film manufactured by the 55 degrees of ion beam incident angle, and ion beam voltage 150 current-density [V and ion beam] A/cm2 of 30micro.
[Drawing 30] Drawing 30 is drawing showing the relation of the crystal stacking tendency of the manufactured polycrystal thin film with ion beam voltage and ion beam current density.
[Drawing 31] Drawing 31 is a graph which shows the relation between the degree of incident angle of an ion beam, and the full width at half maximum of the obtained polycrystal thin film.
[Description of Notations]
A — Base material B — Polycrystal thin film C — Oxide superconductivity layer,
K, K' — Grain-boundary inclination theta — The degree of incident angle phi — Angle of rotation

11 — Base-material electrode holder 12 — Target 13 — Ion gun,
20 — crystal grain 22 — oxide superconductivity — conductor 23 — crystal grain,

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[Translation done.]

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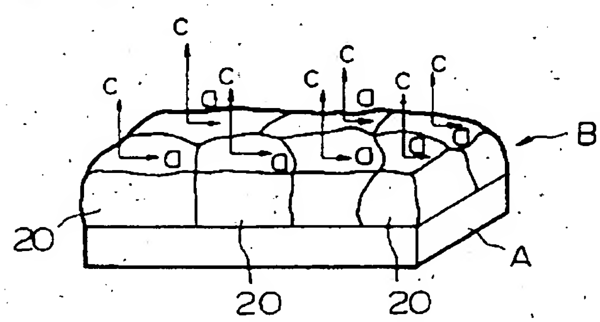
(54)【発明の名称】　多結晶薄膜の製造方法および酸化物超電導導体の製造方法

(57)【要約】

【目的】　本発明は、基材の成膜面に対して直角向きに結晶軸のc軸を配向させることができ、成膜面と平行な面に沿って結晶粒の結晶軸のa軸とb軸を揃えることができ、結晶配向性に優れた多結晶薄膜を提供することを目的とする。

【構成】　本発明は、スパッタリングによりターゲットの構成粒子を叩き出して基材上に堆積させ、基材上に多結晶薄膜を形成する方法において、前記構成粒子を基材上に堆積させる際に、イオン源が発生させたイオンビームを基材の成膜面に対して斜め方向から50～60度の範囲の入射角度で照射しながら前記構成粒子を基材上に堆積させるものである。

【効果】　本発明は構成粒子を効率的に活性化できる結果、基材の成膜面に対してc軸配向性に加えてa軸配向性とb軸配向性をも向上させた粒界傾角30度以下の多結晶薄膜を得ることができる。



【特許請求の範囲】

【請求項１】 スパッタリングによりターゲットの構成粒子を叩き出して基材上に堆積させ、基材上に多結晶薄膜を形成する方法において、前記構成粒子を基材上に堆積させる際に、イオン源が発生させたイオンビームを基材の成膜面に対して斜め方向から５０～６０度の範囲の入射角度で照射しながら前記構成粒子を基材上に堆積させることを特徴とする多結晶薄膜の製造方法。

【請求項２】 スパッタリングによりターゲットの構成粒子を叩き出して基材上に堆積させ、基材上に多結晶薄膜を形成する方法において、前記構成粒子を基材上に堆積させる際に、イオン源が発生させたイオンビームを基材の成膜面に対して斜め方向から照射しながら前記構成粒子を基材上に堆積させるとともに、前記イオンビームの電流密度を２０μＡ／ｃm^2以上、イオンビーム電圧を１５０Ｖ以上で７００Ｖ未満とすることを特徴とする多結晶薄膜の製造方法。

【請求項３】 請求項１記載の多結晶薄膜の製造方法において、イオンビームの入射角度を５５～６０度の範囲に設定して基材上に形成される多結晶薄膜の結晶粒の粒界傾角を２５度以内とすることを特徴とする多結晶薄膜の製造方法。

【請求項４】 請求項１、２または３記載のイオンとして、不活性ガスイオン、あるいは、不活性ガスと酸素ガスの混合イオンを用いることを特徴とする酸化物超電導導体の製造方法。

【請求項５】 スパッタリングによりターゲットの構成粒子を叩き出して基材上に堆積させ、基材上に多結晶薄膜を形成し、次いでこの多結晶薄膜上に酸化物超電導層を形成する酸化物超電導導体の製造方法において、
前記構成粒子を基材上に堆積させる際に、イオン源が発生させたイオンビームを基材の成膜面に対して斜め方向から５０～６０度の範囲の入射角度で照射しつつスパッタ粒子を堆積させて多結晶薄膜を形成し、この多結晶薄膜上に酸化物超電導層を形成することを特徴とする酸化物超電導導体の製造方法。

【請求項６】スパッタリングによりターゲットの構成粒子を叩き出して基材上に堆積させ、基材上に多結晶薄膜を形成し、次いでこの多結晶薄膜上に酸化物超電導層を形成する酸化物超電導導体の製造方法において、前記構成粒子を基材上に堆積させる際に、イオン源が発生させたイオンビームを基材の成膜面に対して斜め方向から照射しつつスパッタ粒子を堆積させるとともに、前記イオンビームの電流密度を２０μＡ／ｃm^2以上、イオンビーム電圧を１５０Ｖ以上で７００Ｖ未満として多結晶薄膜を形成し、この多結晶薄膜上に酸化物超電導層を形成することを特徴とする酸化物超電導導体の製造方法。

【請求項７】 請求項５または６記載の酸化物超電導導体の製造方法において、イオンビームの入射角度を５５～６０度の範囲に設定して基材上に形成される多結晶薄膜の結晶粒の粒界傾角を２５度以内とすることを特徴とする酸化物超電導導体の製造方法。

【請求項８】 請求項５、６または７記載の多結晶薄膜上に酸化物超電導層を形成する際に、多結晶薄膜の結晶に対して酸化物超電導体の結晶をエピタキシャル成長させることを特徴とする酸化物超電導導体の製造方法。

【請求項９】 イオンとして、不活性ガスイオン、あるいは、不活性ガスと酸素ガスの混合イオンを用いることを特徴とする請求項５、６、７または８記載の酸化物超電導導体の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は結晶方位の整った多結晶薄膜の製造方法と結晶方位の整った酸化物超電導導体の製造方法に関する。

【０００２】

【従来の技術】近年になって発見された酸化物超電導体は、液体窒素温度を超える臨界温度を示す優れた超電導体であるが、現在、この種の酸化物超電導体を実用的な超電導体として使用するためには、種々の解決するべき問題点が存在している。その問題点の１つが、酸化物超電導体の臨界電流密度が低いという問題である。

【０００３】前記酸化物超電導体の臨界電流密度が低いという問題は、酸化物超電導体の結晶自体に電気的な異方性が存在することが大きな原因となっており、特に酸化物超電導体はその結晶軸のａ軸方向とｂ軸方向には電気を流し易いが、ｃ軸方向には電気を流しにくいことが知られている。このような観点から酸化物超電導体を基材上に形成してこれを超電導体として使用するためには、基材上に結晶配向性の良好な状態の酸化物超電導体を形成し、しかも、電気を流そうとする方向に酸化物超電導体の結晶のａ軸あるいはｂ軸を配向させ、その他の方向に酸化物超電導体のｃ軸を配向させる必要がある。

【０００４】従来、基板や金属テープなどの基材上に結晶配向性の良好な酸化物超電導層を形成するために種々の手段が試みられてきた。その１つの方法として、酸化物超電導体と結晶構造の類似したＭｇＯあるいはＳｒＴｉO_3などの単結晶基材を用い、これらの単結晶基材上にスパッタリングなどの成膜法により酸化物超電導層を形成する方法が実施されている。

【０００５】前記ＭｇＯやＳｒＴｉO_3の単結晶基材を用いてスパッタリングなどの成膜法を行なえば、酸化物超電導層の結晶が単結晶基材の結晶を基に結晶成長するために、その結晶配向性を良好にすることが可能であり、これらの単結晶基材上に形成された酸化物超電導層は、数十万～数百万Ａ／ｃm^2程度の十分に高い臨界電流密度を発揮することが知られている。

【０００６】

【発明が解決しようとする課題】ところで、酸化物超電導体を導電体として使用するためには、テープ状などの

長尺の基材上に結晶配向性の良好な酸化物超電導層を形成する必要がある。ところが、金属テープなどの基材上に酸化物超電導層を直接形成すると、金属テープ自体が多結晶体でその結晶構造も酸化物超電導体と大きく異なるために、結晶配向性の良好な酸化物超電導層は到底形成できないものである。しかも、酸化物超電導層を形成する際に行なう熱処理によって金属テープと酸化物超電導層との間で拡散反応が生じて酸化物超電導層の結晶構造が崩れ、超電導特性が劣化する問題がある。

【０００７】そこで従来、金属テープなどの基材上に、スパッタ装置を用いてＭｇＯや$SrTiO_3$などの中間層を被覆し、この中間層上に酸化物超電導層を形成することが行なわれている。ところがこの種の中間層上にスパッタ装置により形成した酸化物超電導層は、単結晶基材上に形成された酸化物超電導層よりもかなり低い臨界電流密度（例えば数千～一万Ａ／cm^2程度）しか示さないという問題があった。これは、以下に説明する理由によるものと考えられる。

【０００８】図９は、金属テープなどの基材１上にスパッタ装置により中間層２を形成し、この中間層２上にスパッタ装置により酸化物超電導層３を形成した酸化物超電導導体の断面構造を示すものである。図９に示す構造において、酸化物超電導層３は多結晶状態であり、多数の結晶粒４が無秩序に結合した状態となっている。これらの結晶粒４の１つ１つを個々に見ると各結晶粒４の結晶のｃ軸は基材表面に対して垂直に配向しているものの、ａ軸とｂ軸は無秩序な方向を向いているものと考えられる。

【０００９】このように酸化物超電導層の結晶粒毎にａ軸とｂ軸の向きが無秩序になると、結晶配向性の乱れた結晶粒界において超電導状態の量子的結合性が失なわれる結果、超電導特性、特に臨界電流密度の低下を引き起こすものと思われる。また、前記酸化物超電導体がａ軸およびｂ軸配向していない多結晶状態となるのは、その下に形成された中間層２がａ軸およびｂ軸配向していない多結晶状態であるために、酸化物超電導層３を成膜する場合に、中間層２の結晶に整合するように酸化物超電導層３が成長するためであると思われる。

【００１０】ところで、前記酸化物超電導体の応用分野以外において、多結晶体の基材上に各種の配向膜を形成する技術が利用されている。例えば光学薄膜の分野、光磁気ディスクの分野、配線基板の分野、高周波導波路や高周波フィルタ、空洞共振器などの分野であるが、いずれの技術においても基材上に膜質の安定した配向性の良好な多結晶薄膜を形成することが課題となっている。即ち、多結晶薄膜の結晶配向性が良好であるならば、その上に形成される光学薄膜、磁性薄膜、配線用薄膜などの質が向上するわけであり、更に基材上に結晶配向性の良好な光学薄膜、磁性薄膜、配線用薄膜などを直接形成できるならば、なお好ましい。

【００１１】また、高周波数帯域で使用される磁気ヘッドのコア材として、高透磁率を有し、熱的にも安定なパーマロイ、あるいは、センダストなどの磁性薄膜が実用化されている。これらの磁性薄膜は、従来、蒸着やスパッタにより所定の基板上に形成されるが、これらの磁性薄膜の結晶方位の配向性が低いものであると、磁性薄膜の磁気異方性の制御が困難になり、膜面内では結晶粒の方位が無秩序になり、透磁率の高周波特性が損なわれる問題があった。また、膜面内での結晶軸の軸方向が無秩序であると、面内磁化にスキューやリップルと呼ばれる局所的なゆらぎが発生し、前述のように透磁率の高周波特性が損なわれることになる。

【００１２】本発明は前記課題を解決するためになされたもので、基材の成膜面に対して直角向きに結晶軸のｃ軸を配向させることができると同時に、成膜面と平行な面に沿って結晶粒の結晶軸のａ軸およびｂ軸をも揃えることができ、結晶配向性に優れた多結晶薄膜を提供すること、および、結晶配向性に優れた酸化物超電導層を備えた酸化物超電導導体を提供することを目的とする。

【００１３】

【課題を解決するための手段】請求項１記載の発明は前記課題を解決するために、スパッタリングによりターゲットの構成粒子を叩き出して基材上に堆積させ、基材上に多結晶薄膜を形成する方法において、前記構成粒子を基材上に堆積させる際に、イオン源が発生させたイオンビームを基材の成膜面に対して斜め方向から５０～６０度の範囲の入射角度で照射しながら前記構成粒子を基材上に堆積させるものである。

【００１４】請求項２記載の発明は前記課題を解決するために、スパッタリングによりターゲットの構成粒子を叩き出して基材上に堆積させ、基材上に多結晶薄膜を形成する方法において、前記構成粒子を基材上に堆積させる際に、イオン源が発生させたイオンビームを基材の成膜面に対して斜め方向から照射しながら前記構成粒子を基材上に堆積させるとともに、前記イオンビームの電流密度を２０μＡ／cm^2以上、イオンビーム電圧を１５０以上で７００Ｖ未満とするものである。

【００１５】請求項３記載の発明は前記課題を解決するために、請求項１記載の多結晶薄膜の製造方法において、イオンビームの入射角度を５５～６０度の範囲に設定して基材上に形成される多結晶薄膜の結晶粒の粒界傾角を２５度以内とするものである。

【００１６】請求項４記載の発明は前記課題を解決するために、請求項１または２記載のイオンとして、不活性ガスイオン、あるいは、不活性ガスと酸素ガスの混合イオンを用いるものである。

【００１７】請求項５記載の発明は前記課題を解決するために、スパッタリングによりターゲットの構成粒子を叩き出して基材上に堆積させ、基材上に多結晶薄膜を形成し、次いでこの多結晶薄膜上に酸化物超電導層を形成

する酸化物超電導導体の製造方法において、前記構成粒子を基材上に堆積させる際に、イオン源が発生させたイオンビームを基材の成膜面に対して斜め方向から５０～６０度の範囲の入射角度で照射しつつスパッタ粒子を堆積させて多結晶薄膜を形成し、この多結晶薄膜上に酸化物超電導層を形成するものである。

【００１８】請求項６記載の発明は前記課題を解決するために、スパッタリングによりターゲットの構成粒子を叩き出して基材上に堆積させ、基材上に多結晶薄膜を形成し、次いでこの多結晶薄膜上に酸化物超電導層を形成する酸化物超電導導体の製造方法において、前記構成粒子を基材上に堆積させる際に、イオン源が発生させたイオンビームを基材の成膜面に対して斜め方向から照射しつつスパッタ粒子を堆積させるとともに、前記イオンビームの電流密度を２０μＡ／ｃｍ^{2}以上、イオンビーム電圧を１５０以上で７００Ｖ未満として多結晶薄膜を形成し、この多結晶薄膜上に酸化物超電導層を形成するものである。

【００１９】請求項７記載の発明は前記課題を解決するために、請求項５または６記載の酸化物超電導導体の製造方法において、イオンビームの入射角度を５５～６０度の範囲に設定して基材上に形成される多結晶薄膜の結晶粒の粒界傾角を２５度以内とするものである。

【００２０】請求項８記載の発明は前記課題を解決するために、請求項５、６または７記載の多結晶薄膜上に酸化物超電導層を形成する際に、多結晶薄膜の結晶に対して酸化物超電導体の結晶をエピタキシャル成長させることを特徴とする酸化物超電導体の製造方法。

【００２１】請求項９記載の発明は前記課題を解決するために、イオンとして、不活性ガスイオン、あるいは、不活性ガスと酸素ガスの混合イオンを用いることを特徴とする請求項５、６、７または８記載の酸化物超電導体の製造方法。

【００２２】

【作用】スパッタリングによりターゲットから叩き出したスパッタ粒子を基材上に堆積させる際に、基材の斜め方向５０～６０度の範囲からイオンビームも同時に照射するので、構成粒子が効率的に活性化される結果、基材の成膜面に対してｃ軸配向性に加えてａ軸配向性とｂ軸配向性も向上する。その結果、結晶粒界が多数形成された多結晶薄膜であっても、結晶粒ごとのａ軸配向性とｂ軸配向性とｃ軸配向性のいずれもが良好になり、膜質の向上した多結晶薄膜が得られる。また、スパッタの際の構成粒子を活性化するには、アルゴンイオンまたはアルゴンイオンと酸素イオンの混合イオンが好ましい。

【００２３】なお、前記多結晶薄膜の結晶配向性が整う要因として本発明らは、以下のことを想定している。基板上に形成された立方晶の多結晶薄膜の結晶の単位格子においては、基板法線方向が<１００>軸であり、他の<０１０>軸と<００１>軸は、いずれも、<１００>

軸に直交する方向となる。これらの方向に対し、基板法線に対して斜め方向から入射するイオンビームを考慮すると、単位格子の原点に対して単位格子の対角線方向、即ち、<１１１>軸に沿って入射する場合は５４．７度の入射角度となる。ここで前記のようにイオンビームの入射角度が５０～６０度の範囲で良好な結晶配向性を示すことは、イオンビームの入射角度が前記５４．７度と一致するかその前後になることが関連していると思われ、これらの角度が一致するか、近似した場合にイオンチャンネリングが最も効果的に起こり、基材上に堆積している結晶において、基材の上面で前記角度に一致する配置関係になった原子のみが選択的に残り易くなり、その他の乱れた原子配列のものは斜めに入射されるイオンビームが発生させるスパッタ効果によりスパッタされて除去される結果、配向性の良好な原子の集合した結晶のみが選択的に残って堆積し、これが原因となって結晶配向性が整うものと推定している。

【００２４】従ってイオンビーム電圧は低過ぎるとイオン照射不足になって前記効果を生じにくくし、高すぎると逆にスパッタ効果を生じて結晶配向性を乱してしまうことになる。以上のことから、イオンビームの電流密度は２０μＡ／ｃｍ^{2}以上とすることが好ましく、イオンビーム電圧は１５０Ｖ以上で７００Ｖ未満とすることが好ましい。

【００２５】また、前記結晶配向性の良好な多結晶薄膜上に酸化物超電導層をエピタキシャル成長させるならば、酸化物超電導層が多結晶薄膜の結晶に沿って結晶成長する結果、酸化物超電導層もａ軸配向性とｂ軸配向性とｃ軸配向性の良好なものが得られる。

【００２６】

【実施例】以下、図面を参照して本発明の実施例について説明する。図１は本発明の多結晶薄膜を基材上に形成した一実施例を示すものであり、図１においてＡは板状の基材、Ｂは基材Ａの上面に形成された多結晶薄膜を示している。前記基材Ａは、例えば板材、線材、テープ材などの種々の形状のものを用いることができ、基材Ａは、銀、白金、ステンレス鋼、銅などの金属材料や合金、あるいは、各種ガラスあるいは各種セラミックスなどからなるものである。

【００２７】前記多結晶薄膜Ｂは、立方晶系の結晶構造を有する微細な結晶粒２０が、多数、相互に結晶粒界を介して接合一体化されてなり、各結晶粒２０の結晶軸のｃ軸は基材Ａの上面（成膜面）に対して直角に向けられ、各結晶粒２０の結晶軸のａ軸どうしおよびｂ軸どうしは、互いに同一方向に向けられて面内配向されている。また、各結晶粒２０のｃ軸が基材Ａの（上面）成膜面に対して直角に配向されている。そして、各結晶粒２０のａ軸（あるいはｂ軸）どうしは、それらのなす角度（図２に示す粒界傾角Ｋ）を３０度以内にして接合一体化されている。

【００２８】次に前記多結晶薄膜Ｂを製造する装置について説明する。図３は前記多結晶薄膜Ｂを製造する装置の一例を示すものであり、この例の装置は、スパッタ装置にイオンビームアシスト用のイオンガンを設けた構成となっている。

【００２９】本例の装置は、基材Ａを水平に保持する基材ホルダ１１と、この基材ホルダ１１の斜め上方に所定間隔をもって対向配置された板状のターゲット１２と、前記基材ホルダ１１の斜め上方に所定間隔をもって対向され、かつ、ターゲット１２と離間して配置されたイオンガン１３と、前記ターゲット１２の下方においてターゲット１２の下面に向けて配置されたスパッタビーム照射装置１４を主体として構成されている。また、図中符号１５は、ターゲット１２を保持したターゲットホルダを示している。

【００３０】また、本実施例の装置は図示略の真空容器に収納されていて、基材Ａの周囲を真空雰囲気に保持できるようになっている。更に前記真空容器には、ガスボンベなどの雰囲気ガス供給源が接続されていて、真空容器の内部を真空などの低圧状態で、かつ、アルゴンガスあるいはその他の不活性ガス雰囲気または酸素を含む不活性ガス雰囲気にすることができるようになっている。

【００３１】なお、基材Ａとして長尺の金属テープ（ハステロイ製あるいはステンレス製などのテープ）を用いる場合は、真空容器の内部に金属テープの送出装置と巻取装置を設け、送出装置から連続的に基材ホルダ１１に基材Ａを送り出し、続いて巻取装置で巻き取ることでテープ状の基材上に多結晶薄膜を連続成膜することができるように構成することが好ましい。前記基材ホルダ１１は内部に加熱ヒータを備え、基材ホルダ１１の上に位置された基材Ａを所用の温度に加熱できるようになっている。また、基材ホルダ１１の底部には角度調整機構Ｄが付設されている。この角度調整機構Ｄは、基材ホルダ１１の底部に接合された上部支持板５と、この上部支持板５にピン結合された下部支持板６と、この下部支持板６を支持する基台７を主体として構成されている。前記上部支持板５と下部支持板６とはピン結合部分を介して互いに回動自在に構成されており、基材ホルダ１１の水平角度を調整できるようになっている。なお、本例では基材ホルダ１１の角度を調整する角度調整機構Ｄを設けたが、角度調整機構Ｄをイオンガン１３に取り付けてイオンガン１３の傾斜角度を調整し、イオンビームの入射角度を調整するようにしても良い。また、角度調整機構は本実施例の構成に限るものではなく、種々の構成のものを採用することができるのは勿論である。

【００３２】前記ターゲット１２は、目的とする多結晶薄膜を形成するためのものであり、目的の組成の多結晶薄膜と同一組成あるいは近似組成のものなどを用いる。ターゲット１２として具体的には、ＭｇＯあるいはY_2O_3で安定化したジルコニア（ＹＳＺ）、ＭｇＯ、$SrTiO_3$などを用いるがこれに限るものではなく、形成しようとする多結晶薄膜に見合うターゲッを用いれば良い。

【００３３】前記イオンガン１３は、容器の内部に、蒸発源を収納し、蒸発源の近傍に引き出し電極を備えて構成されている。そして、前記蒸発源から発生した原子または分子の一部をイオン化し、そのイオン化した粒子を引き出し電極で発生させた電界で制御してイオンビームとして照射する装置である。粒子をイオン化するには直流放電方式、高周波励起方式、フィラメント式、クラスタイオンビーム方式などの種々のものがある。フィラメント式はタングステン製のフィラメントに通電加熱して熱電子を発生させ、高真空中で蒸発粒子と衝突させてイオン化する方法である。また、クラスタイオンビーム方式は、原料を入れたるつぼの開口部に設けられたノズルから真空中に出てくる集合分子のクラスタを熱電子で衝撃してイオン化して放射するものである。本実施例においては、図４（ａ）に示す構成の内部構造のイオンガン１３を用いる。このイオンガン１３は、筒状の容器１６の内部に、引出電極１７とフィラメント１８とＡｒガスなどの導入管１９とを備えて構成され、容器１６の先端からイオンをビーム状に平行に照射できるものである。

【００３４】前記イオンガン１３は、図３に示すようにその中心軸Ｓを基材Ａの上面（成膜面）に対して入射角度θ（基材Ａの垂線（法線）と中心線Ｓとのなす角度）でもって傾斜させて対向されている。この入射角度θは５０～６０度の範囲が好ましいが、５５～６０度の範囲が最も好ましい。従ってイオンガン１３は基材Ａの上面に対して傾斜角θでもってイオンビームを入射できるように配置されている。なお、前記イオンガン１３によって基材Ａに照射するイオンビームは、He^+、Ne^+、Ar^+、Xe^+、Kr^+などの希ガスのイオンビーム、あるいは、それらと酸素イオンの混合イオンビームなどで良い。だだし、多結晶薄膜の結晶構造を整えるためには、ある程度の原子量が必要であり、あまりに軽量のイオンでは効果が薄くなることを考慮すると、Ar^+、Kr^+などのイオンを用いることが好ましい。

【００３５】前記スパッタビーム照射装置１４は、イオンガン１３と同等の構成をなし、ターゲット１２に対してイオンビームを照射してターゲット１２の構成粒子を叩き出すことができるものである。なお、本発明装置ではターゲット１３の構成粒子を叩き出すことができることが重要であるので、ターゲット１２に高周波コイルなどで電圧を印可してターゲット１２の構成粒子を叩き出し可能なように構成し、スパッタビーム照射装置１４を省略しても良い。

【００３６】次に前記構成の装置を用いて基材Ａ上にＹＳＺの多結晶薄膜Ｂを形成する場合について説明する。基材Ａ上に多結晶薄膜Ｂを形成するには、ＹＳＺのターゲットを用いるとともに、角度調整機構Ｄを調節してイ

オンガン１３から照射されるイオンビームを基材ホルダ１１の上面に５０～６０度の範囲の角度で照射できるようにする。次に基材Ａを収納している容器の内部を真空引きして減圧雰囲気とする。そして、イオンガン１３とスパッタビーム照射装置１４を作動させる。

【００３７】スパッタビーム照射装置１４からターゲット１２にイオンビームを照射すると、ターゲット１２の構成粒子が叩き出されて基材Ａ上に飛来する。そして、基材Ａ上に、ターゲット１２から叩き出した構成粒子を堆積させると同時に、イオンガン１３からＡｒイオンと酸素イオンの混合イオンビームを照射する。このイオン照射する際の入射角度θは、５０～６０度が最も好ましい。ここでθを９０度とすると、多結晶薄膜のｃ軸は基材Ａの成膜面に対して直角に配向するものの、基材Ａの成膜面上に（１１１）面が立つので好ましくない。また、θを３０度とすると、多結晶薄膜はｃ軸配向すらしなくなる。前記のような好ましい範囲の角度でイオンビーム照射するならば多結晶薄膜の結晶の（１００）面が立つようになる。

【００３８】このような入射角度でイオンビーム照射を行ないながらスパッタリングを行なうことで、基材Ａ上に形成されるＹＳＺの多結晶薄膜の結晶軸のａ軸とｂ軸とを配向させることができるが、これは、堆積されている途中のスパッタ粒子に対して適切な角度でイオンビーム照射されたことにより効率的に活性化された結果によるものと思われる。

【００３９】なお、この多結晶薄膜Ｂの結晶配向性が整う要因として本発明らは、以下のことを想定している。ＹＳＺの多結晶薄膜Ｂの結晶の単位格子は、図４（ｂ）に示すように立方晶であり、この結晶格子においては、基板法線方向が＜１００＞軸であり、他の＜０１０＞軸と＜００１＞軸はいずれも図４（ｂ）に示す方向となる。これらの方向に対し、基板法線に対して斜め方向から入射するイオンビームを考慮すると、図４（ｂ）の原点Ｏに対して単位格子の対角線方向、即ち、＜１１１＞軸に沿って入射する場合は５４．７度の入射角度となる。ここで前記のように入射角度５０～６０度の範囲で良好な結晶配向性を示すことは、イオンビームの入射角度が前記５４．７度と一致するかその前後になった場合、イオンチャンネリングが最も効果的に起こり、基材Ａ上に堆積している結晶において、基材Ａの上面で前記角度に一致する配置関係になった原子のみが選択的に残り易くなり、その他の乱れた原子配列のものはイオンビームのスパッタ効果によりスパッタされて除去される結果、配向性の良好な原子の集合した結晶のみが選択的に残って堆積してゆくものと推定している。

【００４０】以上のことから、イオンビームを照射する際のイオンビーム電圧は低過ぎるとイオン照射不足になって前記効果を生じにくくし、高すぎると逆にスパッタ効果が高くなって結晶配向性を乱してしまうことになる。以上のことから、イオンビームの電流密度は２０μＡ／ｃｍ^{2}以上とすることが好ましく、イオンビーム電圧は１５０Ｖ以上で７００Ｖ未満とすることが好ましい。

【００４１】図１と図２に、前記の方法でＹＳＺの多結晶薄膜Ｂが堆積された基材Ａを示す。なお、図１では結晶粒２０が１層のみ形成された状態を示しているが、結晶粒２０の多層構造でも差し支えないのは勿論である。

【００４２】次に、図５と図６は本発明に係る酸化物超電導導体の一実施例を示すものであり、本実施例の酸化物超電導導体２３は、板状の基材Ａと、この基材Ａの上面に形成された多結晶薄膜Ｂと、多結晶薄膜Ｂの上面に形成された酸化物超電導層Ｃとからなっている。前記基材Ａと多結晶薄膜Ｂは先の例において説明した材料と同等の材料から構成され、多結晶薄膜Ｂの結晶粒２０は、図１と図２に示すように粒界傾角３０度以内になるように結晶配向されている。

【００４３】次に、酸化物超電導層Ｃは、多結晶薄膜Ｂの上面に被覆されたものであり、その結晶粒２３のｃ軸は多結晶薄膜Ｂの上面に対して直角に配向され、その結晶粒２３…のａ軸とｂ軸は先に説明した多結晶薄膜Ｂと同様に基材上面と平行な面に沿って面内配向し、結晶粒２３どうしが形成する粒界傾角Ｋ'は３０度以内にされている。この酸化物超電導層を構成する酸化物超電導体は、$Y_1Ba_2Cu_3O_x$、$Y_2Ba_4Cu_8O_x$、$Y_3Ba_3Cu_6O_x$なる組成、あるいは$(Bi,Pb)_2Ca_2Sr_2Cu_3O_x$、$(Bi,Pb)_2Ca_2Sr_3Cu_4O_x$なる組成、あるいは、$Tl_2Ba_2Ca_2Cu_3O_x$、$Tl_1Ba_2Ca_2Cu_3O_x$、$Tl_1Ba_2Ca_3Cu_4O_x$なる組成などに代表される臨界温度の高い酸化物超電導体である。

【００４４】次に酸化物超電導層Ｃを形成する装置について説明する。図７は酸化物超電導層を成膜法により形成する装置の一例を示すもので、図７はレーザ蒸着装置を示している。この例のレーザ蒸着装置３０は、処理容器３１を有し、この処理容器３１の内部の蒸着処理室３２に基材Ａとターゲット３３を設置できるようになっている。即ち、蒸着処理室３２の底部には基台３４が設けられ、この基台３４の上面に基材Ａを水平状態で設置できるようになっているとともに、基台３４の斜め上方に支持ホルダ３６によって支持されたターゲット３３が傾斜状態で設けられている。　処理容器３１は、排気孔３７を介して図示略の真空排気装置に接続されて内部を所定の圧力に減圧できるようになっている。

【００４５】前記ターゲット３３は、形成しようとする酸化物超電導層Ｃと同等または近似した組成、あるいは、成膜中に逃避しやすい成分を多く含有させた複合酸化物の焼結体あるいは酸化物超電導体などの板体からなっている。前記基台３４は加熱ヒータを内蔵したもので、基材Ａを所望の温度に加熱できるようになっている。

【００４６】一方、処理容器３１の側方には、レーザ発光装置３８と第１反射鏡３９と集光レンズ４０と第２反射鏡４１とが設けられ、レーザ発光装置３８が発生させたレーザビームを処理容器３１の側壁に取り付けられた透明窓４２を介してターゲット３３に集光照射できるようになっている。レーザ発光装置３８はターゲット３３から構成粒子を叩き出すことができるものであれば、ＹＡＧレーザ、CO_2レーザ、エキシマレーザなどのいずれのものを用いても良い。

【００４７】次に前記ＹＳＺの多結晶薄膜Ｂの上に、酸化物超電導層Ｃを形成する場合について説明する。前記のように基材Ａ上にＹＳＺの多結晶薄膜Ｂを形成したならば、この多結晶薄膜Ｂ上に酸化物超電導層を形成する。酸化物超電導層を多結晶薄膜Ｂ上に形成する場合、この例では図７に示すレーザ蒸着装置３０を使用する。

【００４８】多結晶薄膜Ｂが形成された基材Ａを図７に示すレーザ蒸着装置３０の基台３４上に設置し、蒸着処理室３２を真空ポンプで減圧する。ここで必要に応じて蒸着処理室３２に酸素ガスを導入して蒸着処理室３２を酸素雰囲気としても良い。また、基台３４の加熱ヒータを作動させて基材Ａを所望の温度に加熱する。

【００４９】次にレーザ発光装置３８から発生させたレーザビームを蒸着処理室３２のターゲット３３に集光照射する。これによってターゲット３３の構成粒子がえぐり出されるか蒸発されてその粒子が多結晶薄膜Ｂ上に堆積する。ここで構成粒子の堆積の際に多結晶薄膜Ｂが予めｃ軸配向し、ａ軸とｂ軸でも配向しているので、多結晶薄膜Ｂ上に形成される酸化物超電導層Ｃの結晶のｃ軸とａ軸とｂ軸も多結晶薄膜Ｂに整合するようにエピタキシャル成長して結晶化する。これによって結晶配向性の良好な酸化物超電導層Ｃが得られる。

【００５０】前記多結晶薄膜Ｂ上に形成された酸化物超電導層Ｃは、多結晶状態となるが、この酸化物超電導層Ｃの結晶粒の１つ１つにおいては、図６に示すように基材Ａの厚さ方向に電気を流しにくいｃ軸が配向し、基材Ａの長手方向にａ軸どうしあるいはｂ軸どうしが配向している。従って得られた酸化物超電導層は結晶粒界における量子的結合性に優れ、結晶粒界における超電導特性の劣化が少ないので、基材Ａの面方向に電気を流し易く、臨界電流密度の優れたものが得られる。

【００５１】一方、図８は、多結晶薄膜を製造するための装置の他の例を示すものである。この例の装置において図３に記載した装置と同等の構成部分には同一符号を付してそれらの説明を省略する。この例の装置において図３に示す装置と異っているのは、ターゲット１２を３個設け、スパッタビーム照射装置１４を３個設け、基材Ａとターゲット１２に高周波電源２９を接続した点である。

【００５２】この例の装置では、３個のターゲット１２、１２、１２から、それぞれ別種の粒子を叩き出して基材Ａ上に堆積させて複合膜を形成することができるので、より複雑な組成の多結晶膜でも製造できる特徴がある。また、高周波電源３０を作動させてターゲット１２からスパッタすることもできる。この例の装置を用いて前記方法を実施する場合も図３に示す装置の場合と同様に配向性に優れた多結晶薄膜を得ることができる。

【００５３】（製造例）図３に示す構成の装置を使用し、この装置を収納した容器内部を真空ポンプで真空引きして3.0×10^{-4}トールに減圧した。基材は、幅１０mm、厚さ０.５mm、長さ１０ｃｍのハステロイＣ２７６テープを使用した。ターゲットはＹＳＺ（安定化ジルコニア）製のものを用い、スパッタ電圧１０００Ｖ、スパッタ電流１００ｍＡ、イオン源のビームの入射角度を５５度に設定し、イオン源のアシスト電圧を３００Ｖに、イオンビームの電流密度を１０～７０μＡ／cm^2にそれぞれ設定して基材上にスパッタリングと同時にイオン照射を行なって厚さ０．３μｍの膜状のＹＳＺ層を形成した。ここで前記イオンビームの電流密度とは、試料近くに接地した電流密度計測装置の計測数値によるものである。

【００５４】得られた各ＹＳＺの多結晶薄膜試料についてＣｕＫα線を用いたθ－２θ法によるＸ線回折試験を行なった。図１０～図１３は、イオン源の入射角５５度、イオンビーム電圧３００Ｖでイオンビームの電流密度を１０μＡ／cm^2、２０μＡ／cm^2、４０μＡ／cm^2、７０μＡ／cm^2にそれぞれ測定した試料の回折強さを示す図である。図１０～図１３に示す結果から、イオンビームの電流密度を２０～７０μＡ／cm^2に設定した試料では、ＹＳＺの（２００）面あるいは（４００）面のピークが認められ、ＹＳＺの多結晶薄膜の（１００）面が基材表面と平行な面に沿って配向しているものと推定することができ、ＹＳＺの多結晶薄膜がそのＣ軸を基材上面に垂直に配向させて形成されていることが判明した。なお、図１０に示す結果から、イオンビーム電流密度を１０μＡ／cm^2とした試料にあってはＹＳＺのピークが見られない。よってイオンビーム電流密度が低過ぎると多結晶薄膜の結晶配向性の制御ができないことが判明した。

【００５５】続いて図１４～図１７は、前記の各試料における極点図を示すものである。これらの図からも明らかなように、イオンビームの電流密度を１０μＡ／cm^2とした試料ではｃ軸配向性が見られず、図１０～図１３に示す結果と同等の結果が得られた。以上のことから、イオンビームを照射する際の電流密度は２０μＡ／cm^2以上必要であることが明らかになった。

【００５６】図１８～図２０は、イオン源の入射角度９０度でイオンビーム電圧とイオンビーム電流を適宜変更して測定した試料の回折強さを示す図である。ここで各図に示すビーム電流とは実験に用いたイオンガンの負荷用電流を示している。図１８～図２０に示す結果から、

イオン源の入射角度を９０度に設定してもＹＳＺの（２００）ピークと（４００）ピークを認めることができ、ｃ軸配向性に関しては十分な配向性が認められた。

【００５７】次に、前記のようにｃ軸配向された各試料において、ＹＳＺ多結晶薄膜のａ軸あるいはｂ軸が配向しているか否かを測定した。その測定のためには、図２１に示すように、基材Ａ上に形成されたＹＳＺの多結晶薄膜にＸ線を角度θで照射するとともに、入射Ｘ線を含む鉛直面において、入射Ｘ線に対して２θ（５８．７度）の角度の位置にＸ線カウンター２５を設置し、入射Ｘ線を含む鉛直面に対する水平角度φの値を適宜変更して、即ち、基材Ａを図２１において矢印に示すように回転角φだけ回転させることにより得られる回折強さを測定することにより多結晶薄膜Ｂのａ軸どうしまたはｂ軸どうしの配向性を計測した。その結果を図２２と図２３に示す。

【００５８】図２２に示すようにイオンビームの入射角度を５５度に設定して製造した試料の場合、回折ピークが表われず、φを９０度と０度とした場合、即ち、回転角φに対して９０度おきにＹＳＺの（３１１）面のピークが現われている。これは、基板面内におけるＹＳＺの（０１１）ピークに相当しており、ＹＳＺ多結晶薄膜のａ軸どうしまたはｂ軸どうしが配向していることが明らかになった。これに対し、図２３に示すように、イオンビーム入射角度を９０度に設定して製造した試料の場合、特別なピークが見られず、ａ軸とｂ軸の方向は無秩序になってることが判明した。

【００５９】以上の結果から前記装置によって製造された試料の多結晶薄膜は、ｃ軸配向は勿論、ａ軸どうし、および、ｂ軸どうしも配向していることが明らかになった。よって配向性に優れたＹＳＺなどの多結晶薄膜を製造できることが明らかになった。

【００６０】一方、図２４は、図２２で用いたＹＳＺ多結晶薄膜の試料を用い、この試料の多結晶層の各結晶粒における結晶配向性を試験した結果を示す。この試験では、図２１を基に先に説明した方法でＸ線回折を行なう場合、φの角度を－１０度～４５度まで５度刻みの値に設定した際の回折ピークを測定したものである。図２４に示す結果から、得られたＹＳＺの多結晶薄膜の回折ピークは、粒界傾角３０度以内では表われるが、４５度では消失していることが明らかである。従って、得られた多結晶薄膜の結晶粒の粒界傾角は、３０度以内に収まっていることが判明し、良好な配向性を有することが明らかになった。

【００６１】次に前記の製造条件とほぼ同等の条件でイオンビーム電圧を５００Ｖ、７００Ｖ、２００Ｖ、１５０Ｖのそれぞれの値に設定し、イオンビームの電流密度を４０μＡ／ｃｍ^2、５０μＡ／ｃｍ^2、２０μＡ／ｃｍ^2、３０μＡ／ｃｍ^{2}のそれぞれの値に設定して製造した試料についてＸ線回折試験を行なった。それらの結果を図２５～図２９に示す。

【００６２】また、図２５～図２９に示す試験結果から得られた前記のようなイオンビーム電圧およびイオンビーム電流密度の関係と、多結晶薄膜の結晶配向性の関連性を図３０に示す。図３０に示す結果から、イオンビーム電圧とイオンビーム電流密度はいずれも高過ぎても低過ぎても不適であり、イオンビーム電圧は１５０Ｖ以上であって７００Ｖよりも少ないことが必要であり、かつ、イオンビームの電流密度は２０μＡ／ｃｍ^{2}以上は必要であることが判明した。

【００６３】次に、イオンビーム電圧を３００Ｖ、イオンビームの電流密度を４０μＡ／ｃｍ^2、イオンビームエネルギーを３００ｅＶに設定し、イオンビームの入射角度を０度～６５度まで変更して多結晶薄膜を製造した場合、得られた多結晶薄膜の結晶の（１１１）方向の分布における入射角度と半値全幅の関係を示すものである。なお、前記の半値全値は、得られた各試料について、図１６に示すような極点図を求め、この極点図の中心から図１６に示すような補助線ｅ、ｆを引いた場合に、これらの補助線ｅとｆのなす角度αの半分の角度、即ち、ピーク比半分にて求めた。図３１に示す結果から、イオンビームの入射角度が５０～６０度の範囲で結晶配向性が良好になることが明らかになった。また、特に、イオンビームの入射角度を５５～６０度にすることで、粒界傾角を２５度程度の極小値にできることも明らかになった。

【００６４】次に、前記多結晶薄膜上に図７に示す構成のレーザ蒸着装置を用いて酸化物超電導層を形成した。ターゲットとして、$Y_{0.7}Ba_{1.7}Cu_{3.0}O_{7-x}$なる組成の酸化物超電導体からなるターゲットを用いた。また、蒸着処理室の内部を10^{-6}トールに減圧し、室温にてレーザ蒸着を行なった。ターゲット蒸発用のレーザとして波長１９３ｎｍのＡｒＦレーザを用いた。その後、４００゜Ｃで６０分間、酸素雰囲気中において熱処理した。得られた酸化物超電導体は、幅０．５ｍｍ、長さ１０ｃｍのものである。

【００６５】この酸化物超電導導体を冷却し、臨界温度と臨界電流密度の測定を行なった結果、臨界温度＝９.０Ｋ、　臨界電流密度＝５０００００Ａ／ｃｍ^{2}を示し、極めて優秀な超電導特性を発揮することを確認できた。

【００６６】

【発明の効果】以上説明したように本発明の多結晶薄膜の製造方法によれば、スパッタリングによりターゲットから叩き出した構成粒子を基材に堆積させる際に、斜め方向５０度～６０度の角度でイオンビームを照射するので、構成粒子を効率的に活性化できる結果、基材の成膜面に対してｃ軸配向性に加えてａ軸配向性とｂ軸配向性をも向上させた粒界傾角３０度以下の多結晶薄膜を得ることができる。更に、イオンビームの入射角度を５５～６０度にすることで更に良好に結晶配向性を整えること

ができ、粒界傾角２５度以内の良好な結晶配向性の多結晶薄膜を得ることができる。前記の多結晶薄膜は、それを回転させて得られるＸ線回折の回折ピークが９０度おきに出現するので、多結晶薄膜を構成する結晶粒のａ軸とｂ軸における面内配向性が良好であり、また、そのピークの出現範囲は０～３０度の範囲になるので、粒界傾角が３０度になっていることも明らかである。

【００６７】また、多結晶薄膜の製造時のイオンビームの電流密度を２０μｍＡ／ｃｍ^{2}以上とし、イオンビーム電圧を１５０Ｖ以上、かつ、７００Ｖより少なくすることで、良好な結晶配向性の多結晶薄膜を確実に製造することができる。なお、イオンビームとして用いるイオンは不活性ガスイオンあるいは不活性ガスイオンと酸素ガスの混合イオンが好ましい。

【００６８】次に本発明に係る酸化物超電導体の製造方法によれば、基材上にイオンビームの入射角度５０度～６０度で前記のような結晶配向性の良好な多結晶薄膜を形成し、その上に酸化物超電導層を形成する。前記多結晶薄膜は、それを回転させて得られるＸ線回折の回折ピークが９０度おきに出現するので、多結晶薄膜を構成する結晶粒の面内配向性が良好であり、その上に酸化物超電導層を生成するので結晶配向性の良好な酸化物超電導層を形成できる。よって、酸化物超電導層の結晶粒のａ軸どうしあるいはｂ軸どうしの向きも揃えることができるので、臨界電流密度の高い酸化物超電導導体を得ることができる。更に、イオンビームの入射角度を５５～６０度にすることで更に良好に結晶配向性を整えることができ、粒界傾角２５度以内の良好な結晶配向性の多結晶薄膜を得ることができるので、更に結晶配向性の優れた酸化物超電導導体を得ることができる。

【００６９】また、多結晶薄膜の製造時のイオンビームの電流密度を２０μｍＡ／ｃｍ^{2}以上とし、イオンビーム電圧を１５０Ｖ以上、かつ、７００Ｖより少なくすることで、良好な結晶配向性の多結晶薄膜を確実に製造することができ、これを基に酸化物超電導層を形成することで、臨界電流密度の高い酸化物超電導導体を確実に得ることができる。なお、前記イオンビームとして用いるイオンは不活性ガスイオンあるいは不活性ガスイオンと酸素ガスの混合イオンが好ましい。

【図面の簡単な説明】

【図１】図１は本発明方法により形成された多結晶薄膜を示す構成図である。

【図２】図２は図１に示す多結晶薄膜の結晶粒とその結晶軸方向および粒界傾角を示す拡大平面図である。

【図３】図３は本発明方法を実施して基材上に多結晶薄膜を製造する装置の一例を示す構成図である。

【図４】図４は図３に示す装置のイオン源の一例を示す断面図である。

【図５】図５は図１に示す多結晶薄膜の上に形成された酸化物超電導層を示す構成図である。

【図６】図６は図５に示す酸化物超電導層の結晶粒とその結晶軸方向および粒界傾角を示す拡大平面図である。

【図７】図７は多結晶薄膜上に酸化物超電導層を形成するための装置の一例を示す構成図である。

【図８】図８は本発明装置の他の実施例を示す構成図である。

【図９】図９は従来の装置で製造された多結晶薄膜を示す構成図である。

【図１０】図１０はイオンビーム入射角度５５度、イオンビーム電圧３００Ｖ、イオンビーム電流密度１０μＡ／ｃｍ^{2}で製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図１１】図１１はイオンビーム入射角度５５度、イオンビーム電圧３００Ｖ、イオンビーム電流密度２０μＡ／ｃｍ^{2}で製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図１２】図１２はイオンビーム入射角度５５度、イオンビーム電圧３００Ｖ、イオンビーム電流密度４０μＡ／ｃｍ^{2}で製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図１３】図１３はイオンビーム入射角度５５度、イオンビーム電圧３００Ｖ、イオンビーム電流密度７０μＡ／ｃｍ^{2}で製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図１４】図１４はイオンビーム入射角度５５度、イオンビーム電圧３００Ｖ、イオンビーム電流密度１０μＡ／ｃｍ^{2}で製造した多結晶薄膜の極点図である。

【図１５】図１５はイオンビーム入射角度５５度、イオンビーム電圧３００Ｖ、イオンビーム電流密度２０μＡ／ｃｍ^{2}で製造した多結晶薄膜の極点図である。

【図１６】図１６はイオンビーム入射角度５５度、イオンビーム電圧３００Ｖ、イオンビーム電流密度４０μＡ／ｃｍ^{2}で製造した多結晶薄膜の極点図である。

【図１７】図１７はイオンビーム入射角度５５度、イオンビーム電圧３００Ｖ、イオンビーム電流密度７０μＡ／ｃｍ^{2}で製造した多結晶薄膜の極点図である。

【図１８】図１８はイオンビーム入射角度９０度、イオンビーム電圧３００Ｖ、イオンビーム電流２５ｍＡと４５ｍＡで製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図１９】図１９はイオンビーム入射角度９０度、イオンビーム電圧５００Ｖ、イオンビーム電流１５ｍＡ、２５ｍＡ、３５ｍＡで製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図２０】図２０はイオンビーム入射角度９０度、イオンビーム電圧７００Ｖ、イオンビーム電流２５ｍＡで製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図２１】図２１は多結晶薄膜のａ軸およびｂ軸配向性を調べるために行なった試験を説明するための構成図である。

【図２２】図２２は製造された多結晶薄膜の（３１１）面の回折ピークを示すグラフである。

【図２３】図２３は製造された多結晶薄膜の（３１１）面の回折ピークを示すグラフである。

【図２４】図２４は得られた多結晶薄膜の回転角度５度毎の回折ピークを示すグラフである。

【図２５】図２５はイオンビーム入射角度５５度、イオンビーム電圧５００Ｖ、イオンビーム電流密度４０μＡ／ｃｍ^{2}で製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図２６】図２５はイオンビーム入射角度５５度、イオンビーム電圧７００Ｖ、イオンビーム電流密度４０μＡ／ｃｍ^{2}で製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図２７】図２７はイオンビーム入射角度５５度、イオンビーム電圧２００Ｖ、イオンビーム電流密度５０μＡ／ｃｍ^{2}で製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図２８】図２８はイオンビーム入射角度５５度、イオンビーム電圧２００Ｖ、イオンビーム電流密度２０μＡ／ｃｍ^{2}で製造した多結晶薄膜のＸ線回折結果を示すグラフである。

【図２９】図２９はイオンビーム入射角度5.5度、イオンビーム電圧１５０Ｖ、イオンビーム電流密度３０μＡ／ｃｍ^{2}で製造した多結晶薄膜のＸ線回折結果を示すグラフである。

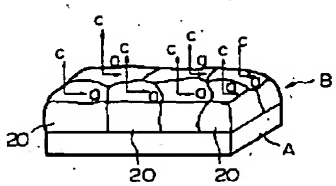
【図３０】図３０はイオンビーム電圧およびイオンビーム電流密度と、製造された多結晶薄膜の結晶配向性の関係を示す図である。

【図３１】図３１はイオンビームの入射角度と得られた多結晶薄膜の半値全幅との関係を示すグラフである。

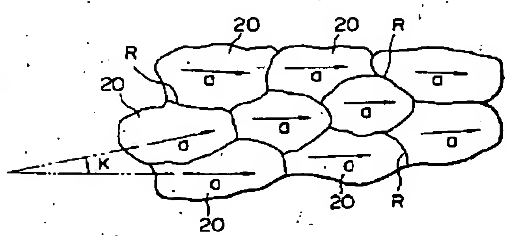
【符号の説明】

Ａ…基材、　Ｂ…多結晶薄膜、
Ｃ…酸化物超電導層、
Ｋ、Ｋ’…粒界傾角、　θ…入射角度、
φ…回転角、
１１…基材ホルダ、　１２…ターゲット、　１３…イオンガン、
２０…結晶粒、　２２…酸化物超電導導体、　２３…結晶粒、

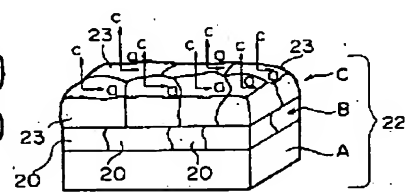
【図１】



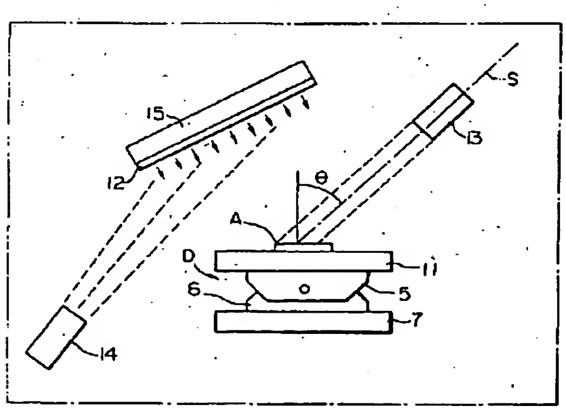
【図２】



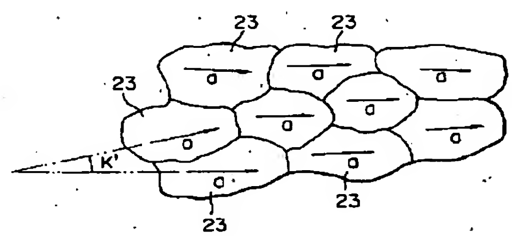
【図５】



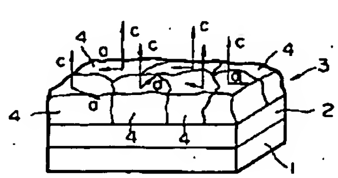
【図３】



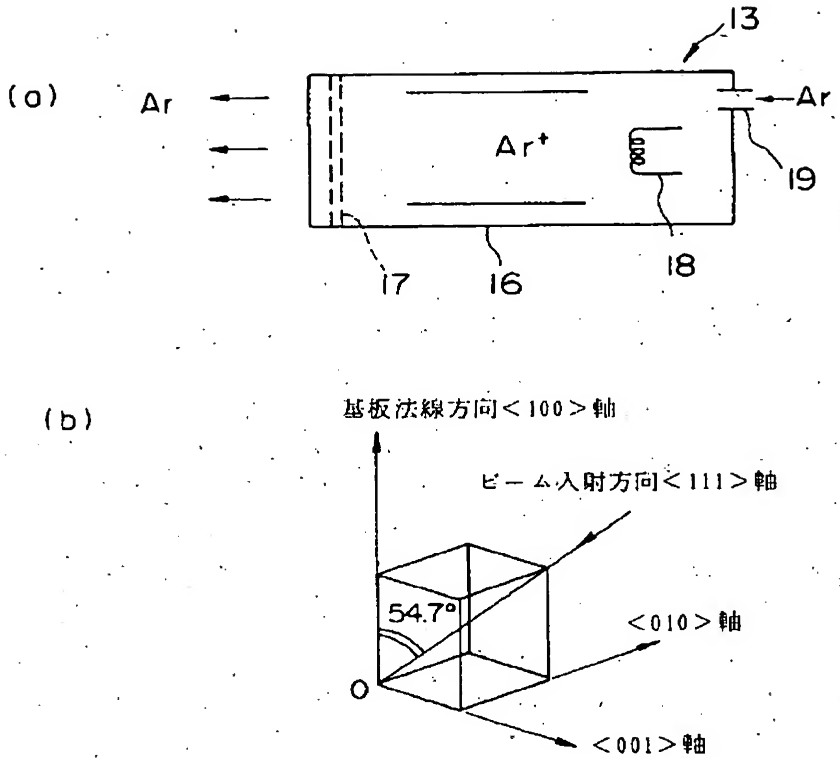
【図６】



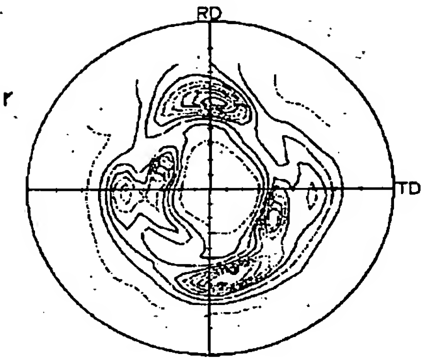
【図９】



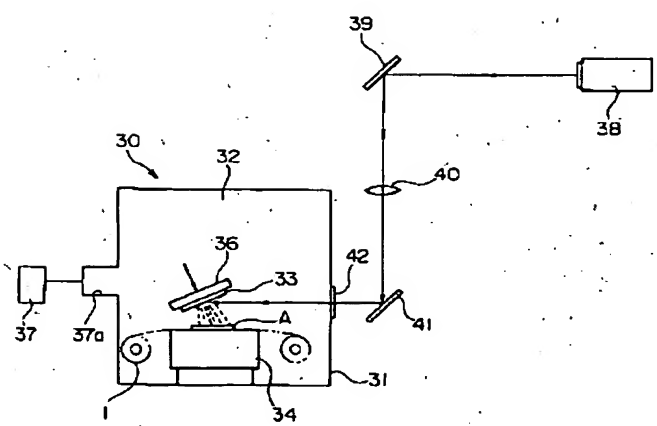
【図4】


(a)
Ar
13
Ar
Ar⁺
19
17
16
18
(b)
基板法線方向＜100＞軸
ビーム入射方向＜111＞軸
54.7°
＜010＞軸
O
＜001＞軸

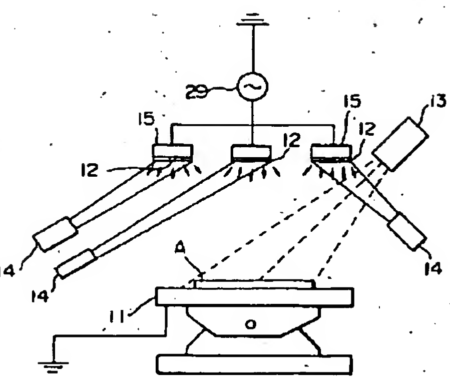
【図14】


RD
TD
300V
10μA／cm²

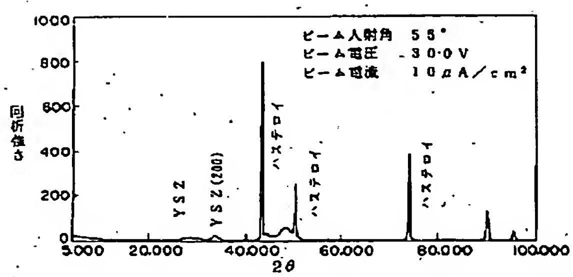
【図7】


39
38
30
32
40
36
33
42
37
37a
A
41
1
34
31

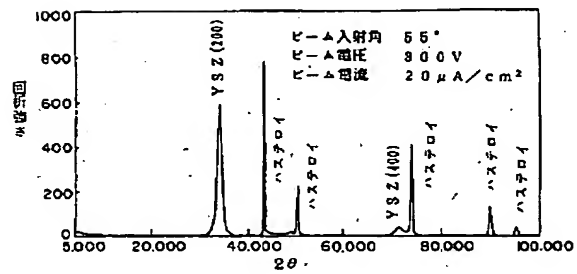
【図8】


29
15
15
13
12
12
12
14
14
14
A
11

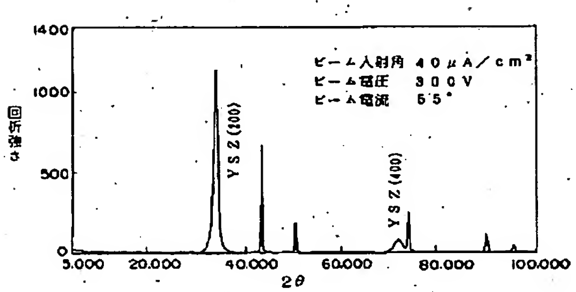
【図１０】



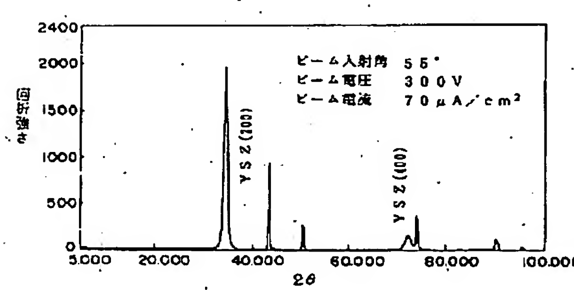
【図１１】



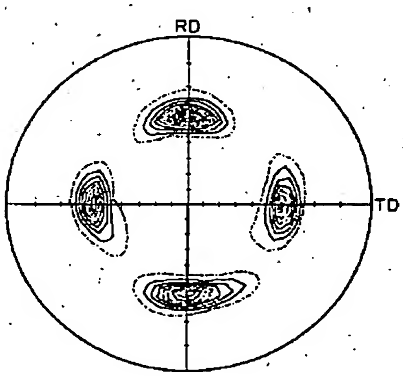
【図１２】



【図１３】

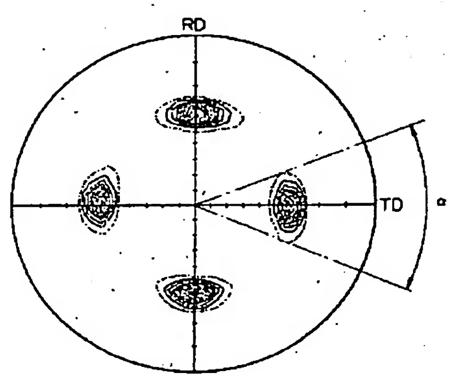


【図１５】



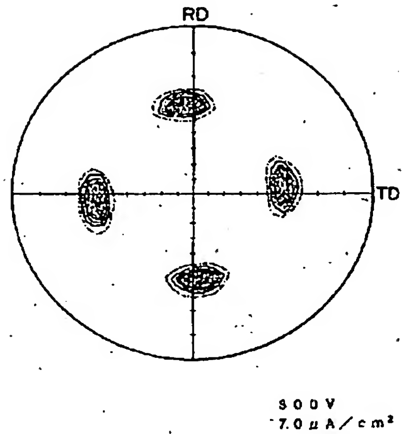
３００Ｖ
２０μＡ／ｃｍ²

【図１６】

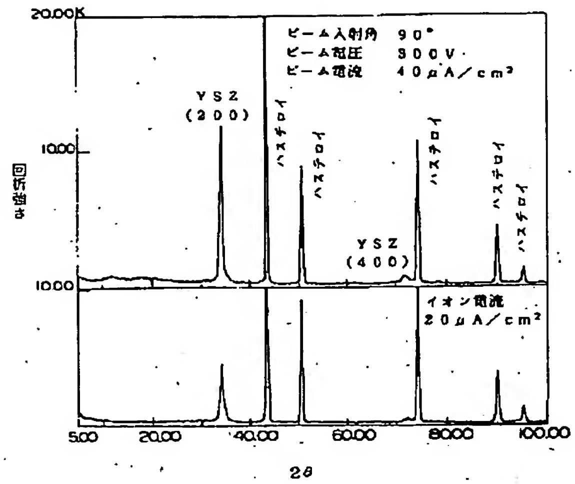


３００Ｖ
４０μＡ／ｃｍ²

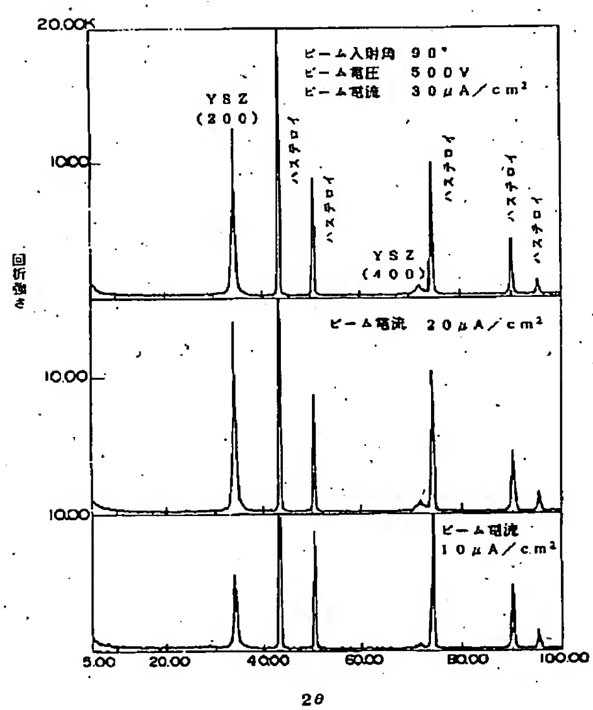
【図17】



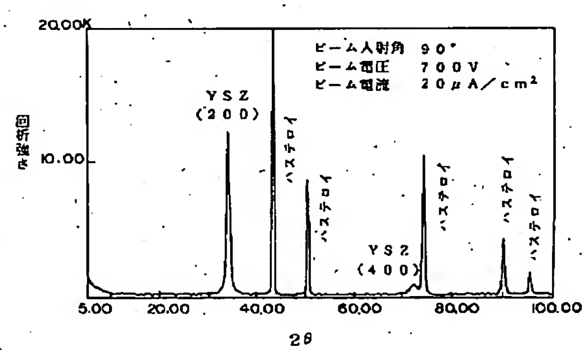
【図18】



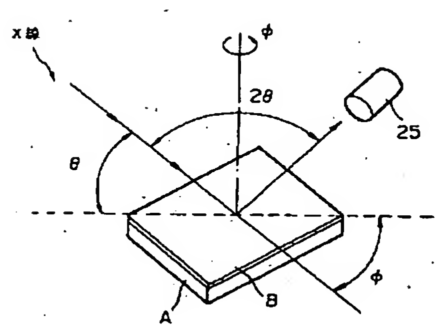
【図19】



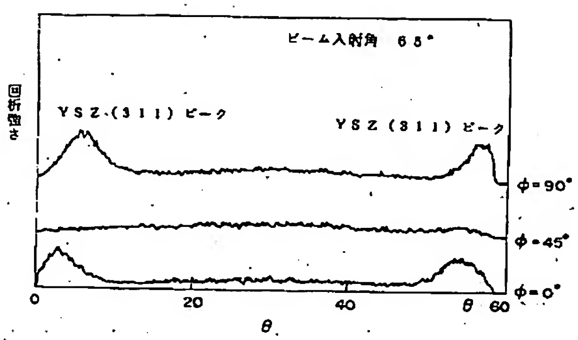
【図20】



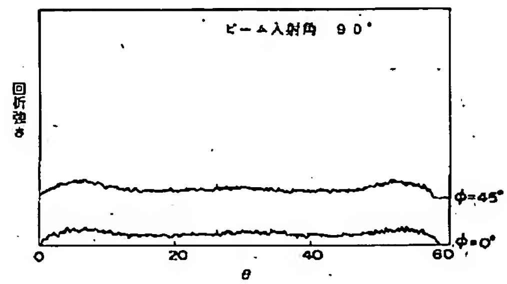
【図21】



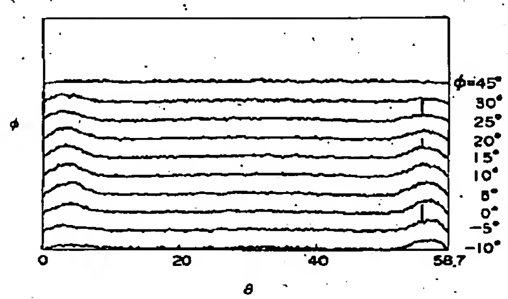
【図２２】



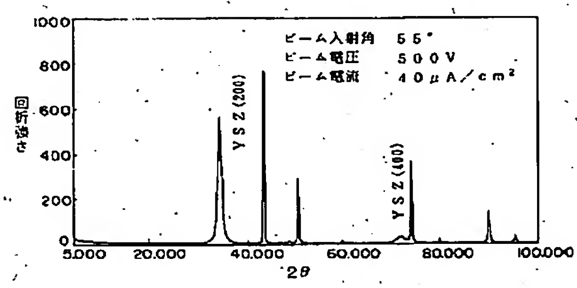
【図２３】



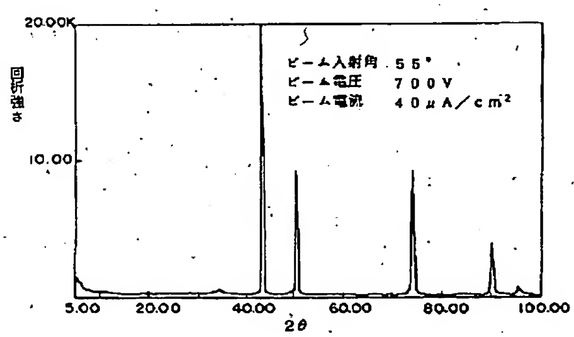
【図２４】



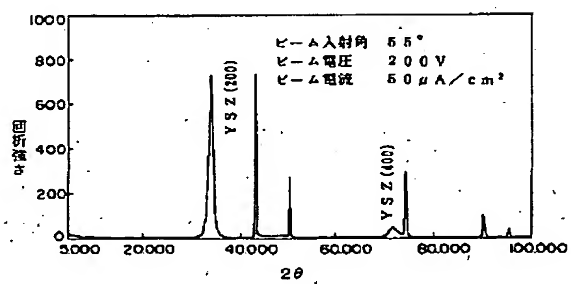
【図２５】



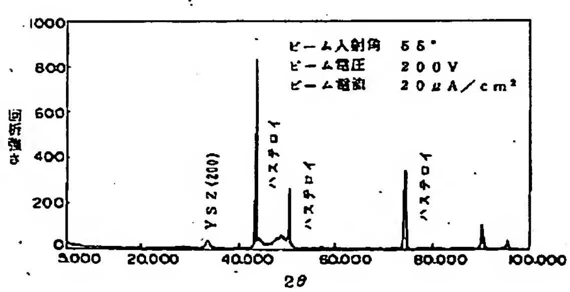
【図２６】



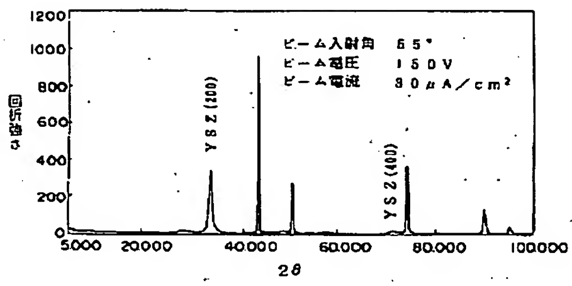
【図２７】



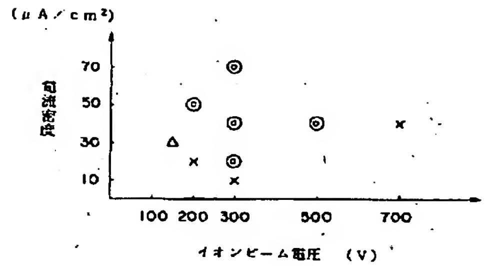
【図２８】



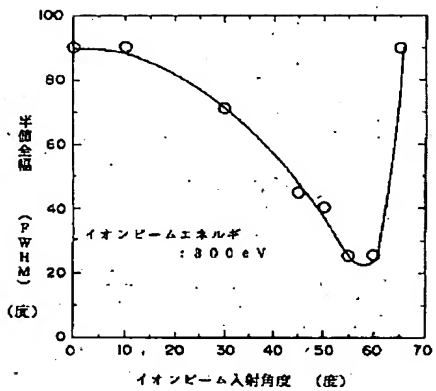
【図29】



【図30】



【図31】



フロントページの続き

(51) Int. Cl.⁵		識別記号		庁内整理番号	F I	技術表示箇所
C23C	14/54			8520－4K		
C30B	29/22	501	H	7821－4G		
H01B	13/00	565	D	7244－5G		
H01L	39/24	ZAA	B	9276－4M		
// H01B	12/06	ZAA		7244－5G		